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XXXV.—THE ALLOYS OF LEAD AND TELLURIUM.

BY HENRY FAY AND C. B. GILLSON.

For several years past, investigations on the chemistry of tellurium have been carried on in the laboratory of this institution. The methods of preparation of pure tellurium[1] and the estimation of tellurium[2] have been studied, and an attempt to determine the atomic weight of tellurium is now in progress. All these problems had been investigated, however, along purely theoretical lines, and it was thought desirable to study the more practical application of the metal, which can now be had in considerable quantities as a waste product in the refining of copper ores. In its physical and chemical properties tellurium is very similar to antimony, and it was thought probable that it might replace antimony in certain alloys. Hence, it was decided to prepare and study the alloys of lead and tellurium.

Recently developed physico-chemical methods have thrown much light on the nature of solutions, and it has been shown that the properties of alloys are entirely analogous to those of solutions. The methods which have been of greatest service in studying the nature of alloys have been the determination of the fusibility curves, and the study of the structure by means of the microscope. These two methods give results which entirely corroborate each other. By the older methods of investigation, such as studies of the heat of formation, heat of solution, electrical conductivity, etc., the different methods not only did not give definite conclusions with regard to the constitution of the alloys, but, in most cases, led to different conclusions. The problem was undoubtedly much more complex than the study of ordinary chemical compounds, since in the latter case it was possible to use solvents which would not affect the nature of the substance when dissolved, whereas, for alloys, there was no solvent which would not entirely change the character of the substances. The work of Le Chatelier, Gautier, Heycock and Neville, Stead, and others has led, however, to definite conclusions, and the fusibility curves established by them have been found to be entirely analogous in character to the curves found for mixtures of simple chemical substances.

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[1] Norris, Fay, and Edgerly: This JOURNAL, **23**, 105.

[2] Norris and Fay: *Ibid.*, **20**, 278.

With the aid of the microscope the results obtained in the determination of the fusibility-curve have been confirmed. The microscope gives an approximate analysis of the different constituents contained in the alloy, and, in many cases, a clue to the order of solidification of the several constituents.

Various alloys composed of two metals have been found to give curves of fusibility, which fall under one of the three following classes, illustrated in the diagrams, Figs. I, II, and III:

1. Two metals which form solid solutions give a straight-line curve connecting the two freezing-points (see Fig. I.). Roozeboom[1] has shown that this curve may have a maximum or a minimum point, but these points may readily be distinguished, by means of the microscope, from maximum points representing compounds, and minimum points corresponding to eutectic alloys.

2. Two metals which form neither solid solutions nor compounds give a curve of two branches meeting in a eutectic,[2]

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[1] J. Phys. Chem., **30**, 385.

[2] The eutectic is that alloy, of definite composition and constant melting-point, in

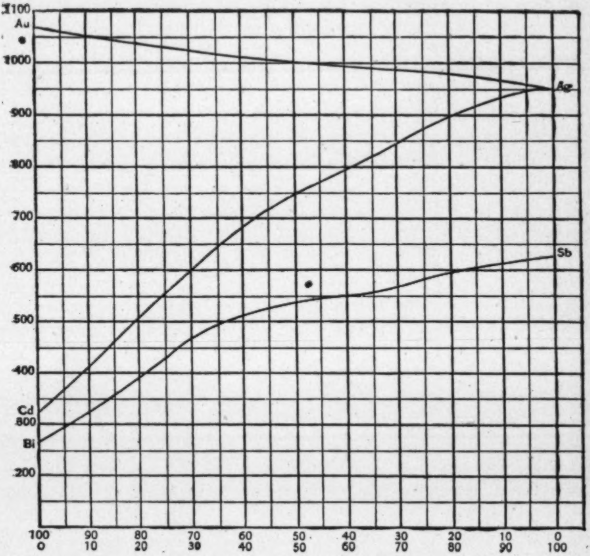

Fig. I.—Diagram showing melting-points of gold-silver, cadmium-silver, and bismuth-antimony alloys. (The ordinates represent degrees C.; the abscissae, percentages of the two constituents of each alloy.)

the freezing-point of which is lower than the freezing-point of either metal (see Fig. II.).

3. Two metals which form one or more compounds give a curve, the number of branches of which is dependent upon the number of compounds formed. In this class one of the compounds may form a solid solution with one of the pure metals, or with another compound (see Fig. III.).

The examples of these classes of alloys, together with their fusibility-curves, shown in Figs. I., II., and III., are offered,

which the constituents are in equilibrium at all temperatures. Its melting-point is lower than the melting-points of its constituents, and its composition is not altered during solidification. The eutectic alloy may be composed of two metals, two compounds, or two solid solutions; a metal and a compound, a metal and a solid solution, or a compound and a solid solution.

not as a complete summary of the work actually accomplished in this field, but merely to illustrate the nature of the work. Many of these curves have been plotted from Gautier's work,[1] and have not been experimentally confirmed.

In Fig. II. the minimum points correspond to the eutectic mixtures; in Fig. III. the maximum points in the curves correspond to definite compounds, and the minimum points to the eutectic alloys.

The study of the microstructure of these three classes of alloys confirms very decisively the fusibility-curves. In the first class it is known that the solvent and dissolved substance separate out together. The microstructure of metals which form solid solutions shows a homogeneous mass, in which it is difficult, if not impossible, to distinguish between the two constituents. The alloys of gold and silver, cadmium and silver, and antimony and bismuth would show on microscopic examination to be composed of homogeneous mixed crystals of the two constituents. In the second class, where the freezing-point of the pure metal is considerably lowered by the addition of the other metal, we know that there is first a separation of pure solvent, and that, as the temperature of the solution is lowered, the pure metal continues to separate until the concentration of the resulting solution has reached that of the eutectic alloy, when the mass solidifies as a whole. The microscopic constituents, consequently, should be the pure metal and the eutectic—the amount of each depending upon the proportion of the two metallic constituents. As the eutectic is the alloy in which the two constituents are mutually saturated, and as the two separate simultaneously, we should expect to find a structure made up of alternate layers of the two metals. This is actually found to be the case, and the structure for all eutectics is very characteristic, resembling the fine-lined markings of the human thumb. The eutectic may consist of two metals, of metal and a compound, or of two compounds; but in all cases its structure is very characteristic and easily recognized. This class of alloys may be illustrated by taking as an example the fusibility-curve of the tin-bismuth alloys, Fig. II. The branch of the curve be-

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[1] Gautier: Bull. Soc. d'Encouragement, 1, 1293 (1896).

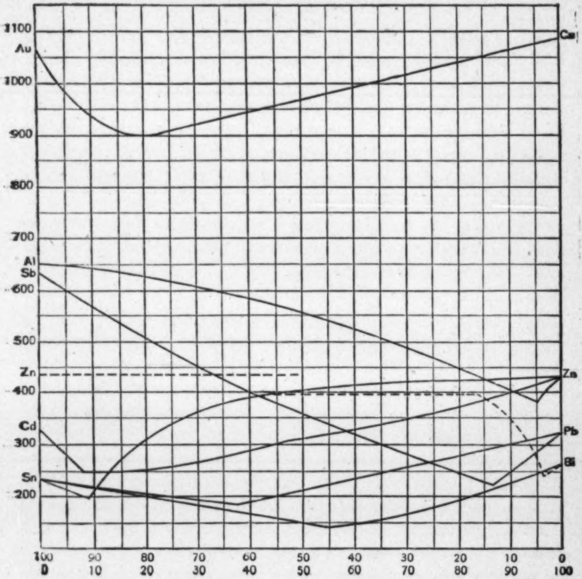

Fig. II.—Diagram showing melting-points of gold-copper, aluminium-zinc, antimony-lead, zinc-bismuth, cadmium-zinc, tin-zinc, tin-lead, and tin-bismuth alloys. (The ordinates represent degrees C.; the abscissae, percentages of the two constituents of each alloy.)

tween 45 and 100 per cent of tin represents the separation of tin and the eutectic of tin and bismuth, the amount of each depending upon the composition. As, by increasing the percentage of bismuth, we approach the composition of the eutectic alloy, 45 per cent tin, more and more of the eutectic structure will appear until the whole mass consists of the eutectic alone. The additions of bismuth to tin have successively lowered its freezing-temperature until, at 55 per cent of bismuth, the lowest freezing-temperature has been reached, and both metals separate simultaneously from solution. With the further addition of bismuth, the freezing-temperatures begin to rise, and the branch of the curve between 55 and 100 per cent of bismuth represents the separation of bismuth (which is now the solvent) and the eutectic alloy, the relative quantities of each being dependent upon the percentage composition. As the composition approaches that of the pure metal, there will evidently be an excess of the pure metal over the eutectic. The presence of compounds of the third class is usually recognized by their crystalline form, the forms of some of them being very characteristic, such as is the case for the compound $SnCu_3$. When, however, a compound forms a solid solution, the detection of the two constituents is much more difficult. To illustrate the third class of alloys we may take, as an example, the alloys of nickel and tin, giving a three-branch curve of fusibility, as determined by Gautier, which is nothing more than a combination of classes 1 and 2. The first class is represented in the branch of the curve between the maximum point at 67 per cent, corresponding to the compound NiSn, and 100 per cent of tin. The microscopic constituents between these two points consist of homogeneous mixed crystals of the compound NiSn and pure tin. The compound forms a eutectic alloy with nickel. Whether we consider the compound NiSn or pure nickel as the solvent, the freezing-point of each is lowered by addition to the other until they are mutually saturated. We then have the eutectic alloy, melting at the lowest possible temperature at which it is possible for a mixture of these two constituents to melt.

The microscopic constituents of the branch between 67 and 100 per cent of nickel consist of pure nickel and the eutectic of nickel and the compound NiSn; between 67 and 33 per cent of the compound and the eutectic.

The Preparation of Pure Tellurium.

The metallic tellurium required was extracted from the slime which is the waste product of the electrolytic process employed at the Baltimore Copper Works in the treatment of copper mattes from the West. This residue, after the removal of silver and copper, consists principally of the sodium salts of silicic, selenous, and tellurous acids, the last named being in large excess. The process by which the necessary liquid

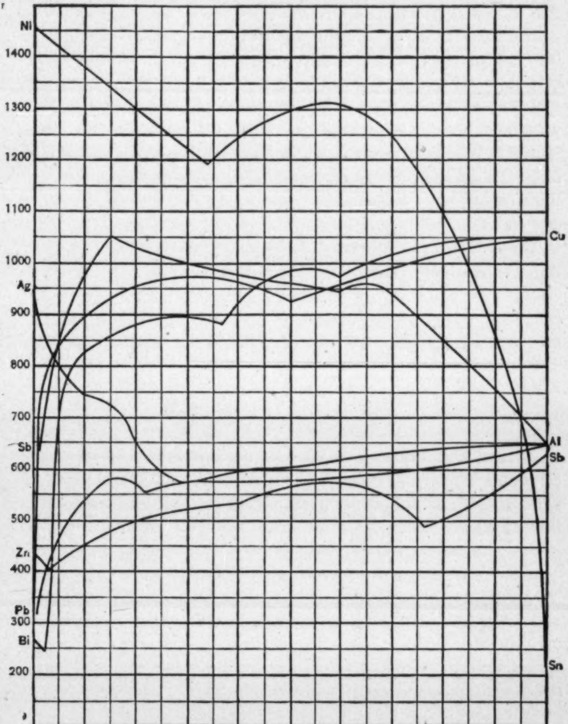

Fig. III.—Diagram showing the melting-points of nickel-tin, silver-aluminium, antimony-copper, zinc-antimony, lead-copper, lead-aluminium, and bismuth-copper alloys. (The ordinates represent degrees C.; the abscissae, percentages of the two constituents of each alloy.)

solution is secured and the copper is refined, has been described by Whitehead,[1] and the separation and preparation of pure tellurium has also been recently described.[2] It will suffice to say here that the method consists in the precipitation of the metal and its conversion into basic tellurium nitrate, $Te_2O_3.(OH).NO_3$. This finely crystallized salt serves as an excellent means of obtaining pure tellurium. The basic nitrate is decomposed by heat; the oxide thus obtained is dissolved in hydrochloric acid, and from this solution the metal is reprecipitated by means of sulphur dioxide. Crystallization of the basic nitrate from a nitric acid solution removes selenium completely from the tellurium, and also furnishes a very convenient method for the separation of other metals.

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[1] J. Am. Chem. Soc., **17**, 280, 848.

[2] This JOURNAL, **23**, 105.

Tellurium thus prepared is a black amorphous powder. After fusion and cooling, however, it is decidedly crystalline, resembling antimony very markedly in this respect, but in luster being nearly as bright and white as silver. It is capable of taking a high polish, but, on account of its brittleness, it is difficult to get an entirely smooth surface. Its freezing-point is 446° C., and its specific gravity 6.243.

The Preparation of the Alloys.

Having obtained in this way about 250 grams of pure tellurium, we made 17 alloys, varying in composition from 98 per cent lead and 2 per cent tellurium to 5 of lead and 95 of tellurium.

The lead used in the experiments was from two different sources, but both samples were as pure as could be obtained. The freezing-point of both samples was found to be 322° C.

In mixing the alloys, granulated tellurium was added to molten lead contained in a porcelain crucible. In every case it was found necessary to add from 2 to 5 per cent more than the amount theoretically required, in order to secure the composition desired. After the metals had been brought together the molten mass was thoroughly stirred, and the heat continued for a few minutes, in order to insure complete fusion. The mass was allowed to cool in the smoky flame of the burner. In all cases, when the two metals were brought together in the crucible, there was an evolution of light and heat, and the mass solidified to a hard cake, which, in some cases, was melted only with the aid of the blast-lamp. This hard mass, as will be shown later, was lead telluride.

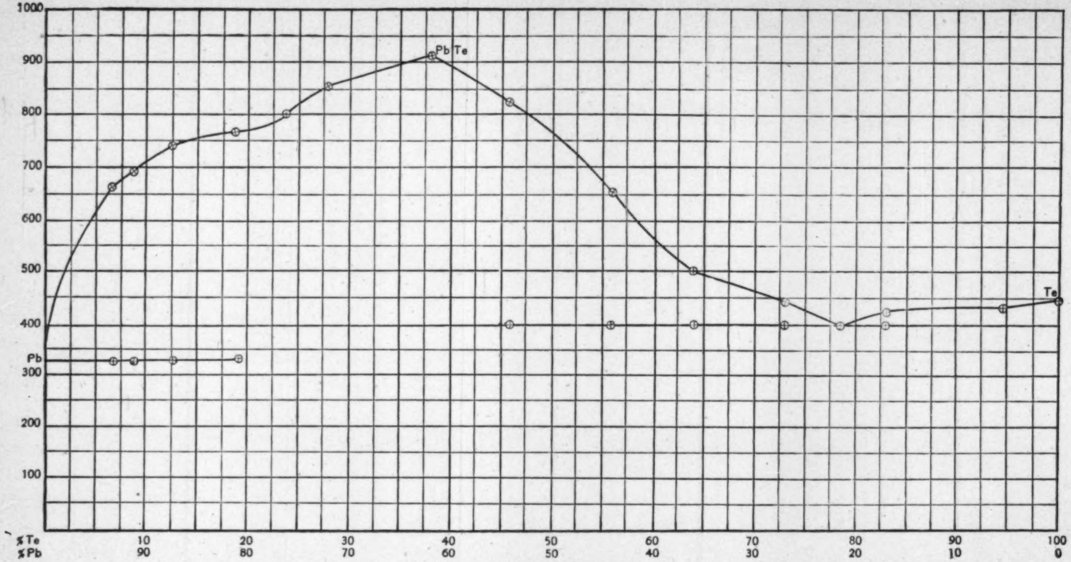

Fig. IV.—Diagram showing lower and higher freezing-points of lead-tellurium alloys. (The ordinates represent degrees C.; the abscissae, percentages of lead and tellurium, respectively.

Throughout the operation the fused metals were protected from oxidation by a layer of finely-powdered charcoal spread over the surface.

The Analysis of the Alloys.

To obtain samples for analysis, a vertical section one-eighth inch thick was sawed out from the mass of each alloy, one-half being used for analysis and the other half for microscopical examination. As the alloys varied considerably in hardness it was possible to pulverize some of them, while from others the sample was obtained by filing.

No reliable procedure was known for the determination of either lead or tellurium in the presence of the other, and many methods were tried without much success. It was thought that tellurium might be separated by taking advantage of the insolubility of its basic nitrate in strong nitric acid, but concordant results were not obtained. It was also found impossible to remove the lead as sulphate, and to precipitate the tellurium from the sulphuric acid filtrate.

The method finally employed for the analysis of all of the alloys consisted in volatilizing the tellurium as chloride, in a current of chlorine gas, and weighing the residue of lead chloride. It was found that by keeping the temperature near the fusing-point of lead chloride, all of the tellurium chloride could be distilled off without loss of lead. This method was found to be very convenient, accurate, and rapid. Table I., showing the tabulated results of the analyses, gives the percentage of lead as found by analysis, and that of tellurium as calculated by difference.

The Determination of the Freezing-Points.

All determinations of freezing-points were made with a Le Chatelier thermo-electric pyrometer. The electric couple of this pyrometer consisted of a pure platinum wire and a wire of platinum alloyed with 10 per cent of rhodium. These wires were soldered to copper-wire leads, connecting them with a galvanometer of the d'Arsonval type, which reflected a beam of light upon a millimeter scale. The junction was calibrated by noting the deflections corresponding to the following known points, stated in centigrade degrees :

	Boiling-points.		Freezing-points.
Water	100	Aluminium	660
Naphthalene	218	Gold	1072
Sulphur	445	Copper	1095

The deflections were such that by reading to tenths of a millimeter one could estimate the temperature within 2° C.

Since both lead and tellurium alloyed very readily with either platinum or platinum-rhodium, it was found necessary to protect the junction. This was satisfactorily effected by threading the wire through a piece of hard-glass tubing of small diameter, bent into a long, narrow U.

In determining the freezing-point of an alloy, the junction was placed in a molten mass, contained in a porcelain crucible, and readings were made every ten seconds during the cooling. In this way the freezing-points given in Table I., and shown graphically in Fig. IV., were determined.

The Microscopical Examination of the Alloys.

Each sample for microscopical examination was one-half of the vertical cross-section, one-eighth inch thick, which had been sawed from the center of the mass of each alloy, the other half of the section having been used for analysis. The surface was first smoothed with a file, and then by rubbing under

Table I.—Freezing-Points and Percentage Composition of Lead-Tellurium Alloys.

(Shown graphically in Fig. IV.)

Alloy. No.	Lead. Per cent.	Tellurium. Per cent.	Lower freezing-point. Deg. C.	Higher freezing-point. Deg. C.
1	100.00	....	...	322
2	94.00	6.00	320	665
3	91.30	8.70	325	695
4	87.50	12.50	322	743
5	81.40	18.60	322	775
6	76.40	23.60	...	805
7	72.20	27.80	...	859
8	61.97	38.03	917	917
9	54.10	45.90	397	828
10	43.70	56.30	400	656
11	35.90	64.10	400	550
12	27.20	72.80	400	445
13	21.50	78.50	400	400
14	17.00	83.00	400	427
15	5.60	94.40	...	433
16	....	100.00	446	446

water on an Arkansas stone. The final polish was accomplished by rubbing very lightly on rouge placed on chamois. The surfaces were all etched with very dilute hot nitric acid, which brought out the structure satisfactorily. The alloys containing not more than 38 per cent of tellurium could be etched by polishing in relief, but the process was laborious and had no particular advantage over etching with nitric acid.

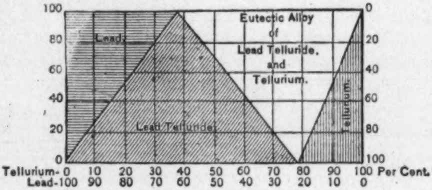
100
80
60
40
20
0
0
20
40
60
80
100
Lead
Lead Telluride
Eutectic Alloy of Lead Telluride, and Tellurium.
Tellurium.
Tellurium- 0 10 20 30 40 50 60 70 80 90 100 Per Cent.
Lead-100 90 80 70 60 50 40 30 20 10 0

Fig. V.—Diagram showing the percentage of each constituent in various lead-tellurium alloys.

All the photographs from which Figs. VI. to XII. have been made, were taken at 95 diameters' magnification, and have been reproduced by the engraver at 80 diameters.

Discussion of Results.

Upon inspection of the freezing-points given in Table I., and shown graphically in Fig. IV., it is seen that the freezing-point of pure lead is raised to a remarkable extent by the addition of small amounts of tellurium. For example, in alloy No. 2 the addition of 6 per cent of tellurium has caused a rise in the freezing-point of over 300° C., but the further addition of tellurium has not caused a proportionate elevation of the freezing-point. The maximum freezing-point, 917° C., was reached when the composition of the alloy corresponded to that of lead telluride, PbTe. The formation of lead telluride explains the evolution of light and heat, and the rapid rise in the freezing-point caused by bringing together the two metals. The metallic lead very easily becomes supersaturated with the lead telluride, and the latter separates out of the solution. As the cooling is carried further, the excess of lead separates. This separation of the two constituents is well shown in the freezing-points of alloys Nos. 3, 4, and 5. The lead point,

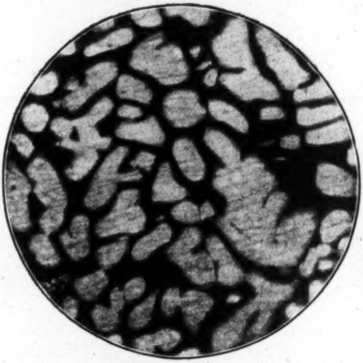

Fig. VI.—Alloy No. 4. Lead and lead telluride.
(80 Diameters.)

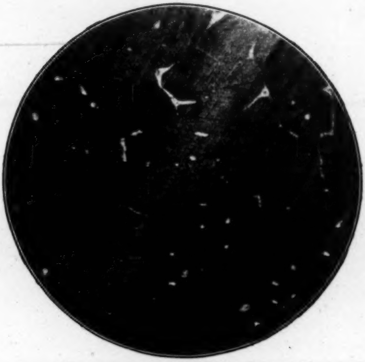

Fig. VII.—Alloy No. 8. Lead telluride.
(80 Diameters.)

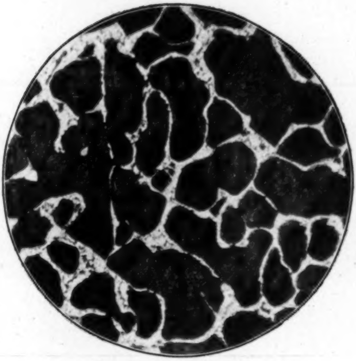

Fig. VIII.—Alloy No. 9. Lead telluride and eutectic.
(80 Diameters.)

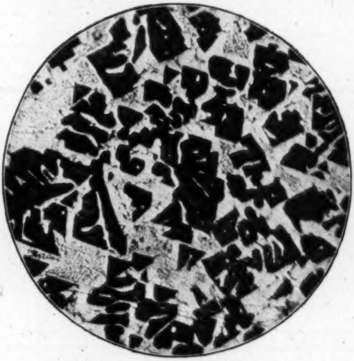

Fig. IX.—Alloy No. 10. Lead telluride and eutectic.
(80 Diameters.)

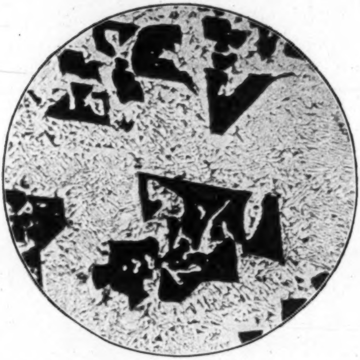

Fig. X.—Alloy No. 11. Lead telluride and eutectic.
(80 Diameters.)

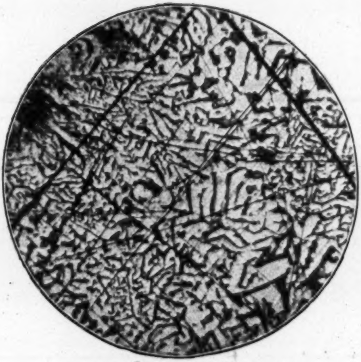

Fig. XI.—Alloy No. 13. Pure eutectic.
(80 Diameters.)

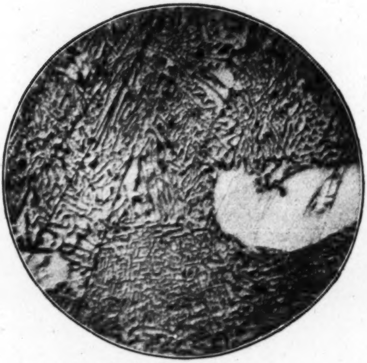

Fig. XII.—Eutectic and tellurium.
(80 Diameters.)

however, disappears or becomes so weak as not to be noticeable, when the tellurium is in excess of 20 per cent. With an increase of tellurium beyond 38 per cent, the freezing-points are lowered, and the fall continues until a temperature of 400° C. is reached.

At this point the alloy solidifies as a whole, and contains 78.50 per cent of tellurium. This alloy is the eutectic of lead telluride and tellurium. The four alloys, Nos. 9, 10, 11, and 12, all showed two points of solidification, corresponding to the separation of lead telluride and the eutectic alloy. The eutectic was prepared in pure condition by allowing alloy No. 11 to solidify partially, and then pouring off the portion remaining liquid. An alloy prepared in this way gives a constant melting-point of 400° C., and shows under the microscope the characteristic eutectic structure shown in Fig. XI.

With increase in the amount of tellurium beyond the eutectic point, the freezing-point gradually rises to that of pure tellurium, 446° C. The freezing-point of tellurium is variously given from 452° to 525° C., but 446° C. has been repeatedly determined on samples, the purity of which was almost beyond question, since, by reason of the method of their preparation, they could not have contained more than mere traces of impurities.

The Microstructure of the Alloys.

The structure of the alloys strongly confirms the curve of fusibility. In Fig. V., constructed from data obtained from the fusibility curve, the composition of any alloy can be seen at a glance. In Fig. IV. it will be seen that the branch of the curve which connects the melting-points of pure lead and lead telluride represents a mixture of lead and lead telluride. The branch connecting the melting-point of lead telluride and the eutectic represents a mixture of these two constituents; the branch from the eutectic point to pure tellurium, a mixture of tellurium and the eutectic alloy. From Fig. V., the percentage-composition of each constituent can be ascertained. For instance, alloy No. 4, melting at 743° C., contains 32 per cent of lead telluride and 68 per cent of lead. This is shown well in Fig VI., where the light constituent is lead and the dark is lead telluride. With 38 per cent of tellurium, the whole mass should consist of lead telluride, and this is shown in Fig. VII., from a photograph of alloy No. 8. The effect of an increase in the amount of tellurium we find in alloy No. 9 (80 per cent of lead telluride and 20 of the eutectic). This is nicely shown in Fig. VIII., where a small amount of the eutectic has made its appearance between the large granules of lead telluride. Fig. IX. represents a photograph from alloy No. 10, containing 46 per cent of eutectic and 54 of lead telluride. The latter is shown as dark crystallites embedded in the eutectic. Alloy No. 11 consists of 68 per cent of eutectic and 32 per cent of lead telluride. A mixture of these two substances in this proportion is shown in Fig. X. Fig. XI. shows a photograph taken from the pure eutectic, made by allowing about two-thirds of one of the alloys to solidify, and then pouring off the still liquid mass. A mixture of the eutectic and an excess of tellurium is shown in Fig. XII. The photographs do not represent exactly the percentages of each constituent, but only approximately. On account of the lead telluride being much lighter than lead, a marked segregation was found in the alloys composed of these two constituents. Lead telluride and the eutectic have nearly the same specific gravity, and consequently show a more homogeneous structure.

It will be seen from the photographs, and from the diagram, Fig. V., that lead telluride is a constituent common to all of the alloys. Its amount gradually increases, as tellurium is added to lead, until the whole mass is lead telluride, and then it gradually decreases until the whole mass is pure tellurium. Tellurium forms a eutectic alloy with lead telluride, but the latter does not form a eutectic alloy with lead. The form of the curve seems to indicate an isomorphous mixture between lead and lead telluride, and the microstructure of the alloys very low in tellurium seem to point in the same direction. But the two constituents differ so widely in fusibility that there is no definite means of knowing whether or not they are really isomorphous. The isomorphism of these two substances seems all the more probable when we take into consideration the fact that the mineral, altaite, PbTe, crystallizes in the isometric system, and it is well known that lead crystallizes in that system.

The hardness of the alloys increases with the amount of tellurium present. The alloys containing over 50 per cent of tellurium are very brittle.

It is proposed to continue this study with other tellurium alloys.

XXXVI.—THE ALLOYS OF ANTIMONY AND TELLURIUM.

BY HENRY FAY AND HARRISON EVERETT ASHLEY.

The study of an entirely new series of alloys may be undertaken from a desire to obtain knowledge applicable to the perfection of industrial alloys, or merely to test certain theoretical considerations. In the case of antimony-tellurium alloys, the theoretical side only is at present important, but it is hoped that the results of this investigation may have some industrial value, at least indirectly, by furnishing one more example for comparison when studying commercial alloys.

The statement is found in various places that antimony is isomorphous with arsenic, bismuth, and tellurium, but very little experimental evidence has been offered in support of this assumption. All four metals crystallize in rhombohedra, and the ratio of the axes $a : c$ is approximately the same—which seems to indicate, but does not prove, their isomorphism. The close association of these metals in minerals also seems to indicate that they are isomorphous. There are, however, certain differences in their properties which render this conclusion somewhat doubtful, and it is therefore desirable that independent evidence be found to decide the question. In a paper on lead-tellurium alloys[1] it has been shown that two metals which are isomorphous give, as a fusibility-curve, a straight line connecting their melting-points. The best examples of this class of alloys are the alloys of gold and silver, gold and platinum, and bismuth and antimony. In each of these cases the properties of the alloys are a mean between the properties of the two metals. The isomorphism of gold and silver and bismuth and antimony might be confirmed by means of the microscope, but, so far as we know, no work has been published on this side of the problem. The microstructure of binary alloys of isomorphous metals should show an intimate mixture of the two metals without any evidence of compounds or of a eutectic mixture. In connection with some work on the isomorphism of selenium and tellurium we had occasion to prepare several bismuth-antimony alloys, in which we found the microstructure to consist of a very homogeneous mixture of the two metals.

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[1] See preceding article.

It was hoped that by taking advantage of the fusibility-curve which could be established by determining the freezing-points of a series of alloys, and by a study of the microscopical appearance of etched specimens of these alloys, we might be able to form some idea in regard to the isomorphism of tellurium and antimony.

With regard to the more practical side of the problem, it might be said that tellurium and antimony are so similar in their physical properties that the former might replace antimony in some of its alloys. If this should be found possible, it would open up a field of usefulness for the large quantities of tellurium which now go to waste. The effect of even small quantities of antimony on malleable metals, such as copper and gold, is most injurious, making them hard and brittle; but, on the other hand, it gives the necessary hardness to the lead of type metal, and produces valuable alloys with tin in Britannia metal for decorative objects, and, with tin, zinc, and copper, Babbitt metal for bearings. With lead, its 12 per cent alloy, the eutectic mixture of these two metals, possesses valuable properties, and is used on account of its power to resist the action of sulphuric acid for making the so-called "lead chambers" for the manufacture of that acid.

Tellurium likewise possesses the power of hardening other metals. This hardening power is very marked in the alloys with lead, and Roberts-Austen has found that it diminishes the tenacity of gold and copper. So far as we know, no ternary alloys containing tellurium, and corresponding to Britannia or Babbitt metals, have been prepared.

Methods and Apparatus.

In order to study the properties of the tellurium-antimony alloys, sufficient of each metal was taken to form a button weighing about 20 grams. In all, fifteen alloys were made, varying from 5 to 95 per cent of tellurium.

The antimony used was the so-called chemically pure metal, which was found to contain traces of lead and sulphur. Its freezing-point[1] was 624° C., and its specific gravity 6.693.

The tellurium was obtained from the residue of the Baltimore Copper Works, and was purified by the method which was recently given in an article on lead-tellurium alloys. Its freezing-point was 446°, and its specific gravity 6.243.

The mixed metals were put in a porcelain crucible, covered with powdered charcoal, fused over the blast-lamp, and allowed to stand until cold. No heat phenomena were noticed during the melting of the two metals.

From the button thus formed a section was sawed out for microscopic examination, and the larger of the remaining portions was used for a specific gravity determination. The two larger parts were then united and used for the freezing-point determination.

Freezing-temperatures of the alloys were measured by means of a thermo-electric junction in connection with a galvanometer of the d'Arsonval type, made by Keiser and Schmidt, of Berlin, and so arranged that readings could be taken by means of a needle passing over a graduated scale. This type of instrument was found to be not nearly so satisfactory for experimental work as a delicately-adjusted reflecting galvanometer. There was considerable lag in the instrument, which could only be obviated by constant tapping; and even by this method we were not sure that our results were correct within 5°. The pyrometer was calibrated against the following substances:

	Degrees C.
Boiling water	100
" naphthalene	218
" sulphur	445
Freezing aluminium	660
" gold	1072

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[1] This freezing-point does not correspond to the value, 630° C., recently determined by Holborn and Day; but the slight difference may be explained by the small amount of impurity in our antimony, and by the lag in the galvanometer.

In order to protect the junction from alloying with the vapors of antimony and tellurium, the two wires were passed through two very small hard-glass tubes, and these tubes were then placed in a larger piece of hard-glass tubing of about 5 mm. diameter.

Freezing-Points.

To determine the freezing-points, the alloys were placed in a Battersea annealing cup and were heated to about 100° above their melting-point. The molten mass, protected from oxidation by a layer of finely divided charcoal, was thoroughly stirred to insure complete admixture of the constituents. The junction was placed vertically in the alloy, and readings of the galvanometer were taken every ten seconds, until the temperature had fallen to 100°. The beginning of the various points of retardation was taken as the freezing-point. The results of these determinations are given in Table I., and are shown graphically in Fig. I.

Table I.—Freezing-Points of Antimony-Tellurium Alloys.

Alloy. No.	Antimony. Per cent.	Tellurium. Per cent.	Higher freezing-temp. Deg. C.	Lower freezing-temp. Deg. C.
1	100	0	624	....
2	95	5	623	....
3	90	10	599	....
4	80	20	568	....
5	75	25	547	....
6	70	30	551	....
7	60	40	561	....
8	50	50	599	....
9	38.63	61.37	629	....
10	30	70	613	422
11	20	80	526	419
12	15	85	434	422
13	10	90	421	....
14	5	95	456	....
15	0	100	446	....

It appears from Fig. I., in which ordinates represent temperatures and abscissae percentage-composition, that the antimony-tellurium alloys belong to the class in which occur one or more definite chemical compounds, and in this respect are similar to the lead-tellurium alloys. The compounds in this class of alloys are always indicated by a maximum point in the fusibility-curve, and by a uniform field when examined under the microscope. In this case it will be seen that the maximum point in the curve corresponds to a freezing-point of 629°, and a composition of 61.37 per cent of tellurium and 38.63 of antimony, which indicates the compound Sb_2Te_3. This compound, antimony telluride, forms a eutectic alloy containing 87 per cent of tellurium, and melting at 421° with tellurium, and is isomorphous with antimony, consequently does not form a eutectic with it. This latter fact places the antimony-tellurium alloys in the sub-class of the third general class of alloys in which one of the compounds is isomorphous with one of the elements. The portion of the curve which connects the freezing-points of antimony and antimony telluride is approximately a straight line, and, considered by itself, represents an isomorphous mixture.

In that part of the curve which is included between 38 and 100 per cent of antimony, we should expect to find, and do find, homogeneous mixed crystals of the pure antimony and antimony telluride. The microscopic field between these two points for all alloys examined is very similar, except where the percentage of antimony is very high, in which case there is some tendency for the telluride to segregate out in masses.

The isomorphism of these two substances seems all the more probable when we consider the fact that the mineral tetradymite, Bi_2Te_3, crystallizes in the rhombohedral system. It is more than likely that the antimony telluride, if it occurred as a mineral, would likewise be found to crystallize in that system. Although tellurium crystallizes in the hexagonal system also, its cleavage indicates that it is not isomorphous with antimony, and consequently not with antimony telluride.

The question might arise as to the existence of a compound of the composition corresponding to the formula SbTe. All we can say at present is that there is no evidence in favor of such a compound. There are no *à priori* reasons why it should not exist, and it is entirely possible that it should exist and form an isomorphous mixture with antimony and antimony telluride, Sb_2Te_3. If it were formed in this mixture we should expect a more marked evolution of heat in the alloys corresponding to this composition, but the amount of heat evolved in the alloy corresponding to this composition was not above the average for the other alloys.

Oppenheim[1] makes the statement that antimony forms either iron-gray, SbTe, or tin-white, Sb_2Te_3. The only evidence, however, in favor of the compound was that the iron-gray mass was homogeneous and had cleavage planes. The assumption seems to have been based on a very small amount of evidence, for the result of our work shows that with these proportions an alloy is formed which, although brittle, homogeneous, and crystalline, is merely an isomorphous mixture of antimony and antimony tritelluride.

From an inspection of the freezing-point curve it seems to be evident that antimony and tellurium are not isomorphous, as has been generally supposed, and that, consequently, they do not mix at the temperature of fusion as such. On the contrary, tellurium and antimony telluride form a series of alloys which in all respects is similar to the class of alloys of which the lead-tin and silver-copper alloys are good examples. In other words, the freezing-point of either antimony tritelluride or of tellurium is lowered by the presence of the other, no matter which one we consider as the solvent. They are mutually soluble and mix in all proportions.

Percentage Composition of the Constituents.

To express approximately the composition of any particular alloy a diagram, Fig. II., has been constructed, which will show at a glance the percentage of each constituent. The abscissae represent the percentages of antimony and tellurium, and the ordinates the division of the total 100 per cent of the alloy into percentages of tellurium and eutectic alloy, antimony telluride, and eutectic alloy, or isomorphous mixture of antimony and antimony telluride. For instance, an alloy whose chemical composition is 40 per cent tellurium and 60 per cent antimony is made up of a mixture of 35 per cent antimony and 65 per cent antimony telluride. Again, if we wish to obtain an alloy containing 34 per cent of eutectic and 66 per cent of antimony telluride, it is readily seen that it must consist of 70 per cent of tellurium and 30 per cent of antimony.

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[1] J. prakt. Chem., 71, 277.

Specific Gravities.

In view of the nature of these alloys, it was thought desirable to study the specific gravities, but from the results obtained no conclusion could be drawn. It seems to be true that nearly all the physical properties of alloys are additive and give no clue to the nature of the constitution. Various values for the specific gravity of tellurium have been given. Rammelsberg found for the amorphous variety the value 5.93 and for the crystalline 6.38 to 6.42. At 0°, Spring[1] found for the uncompressed 6.2322, and for the compressed 6.2549. Later, he reported the value 6.22. Klein and Morel[2] found values varying from 6.204 to 6.215, and, recently, Lenher and Morgan[3] have reported the value 6.1993. Priwoznik[4] obtained the value 6.2549 on a specimen which had been carefully prepared, and which had been fused in a current of hydrogen.

Using a specimen of tellurium which had been prepared from recrystallized basic nitrate, we found the value 6.243. This value represents several actual determinations on specimens known to be pure and free from blow-holes, and is also the average of several other determinations on other specimens. The most accurate determination was made from a button weighing from 30 to 40 grams, which had been fused several times under charcoal. This was split in half, and the outside surfaces were smoothed on an emery wheel. It was suspended in boiling water for some time ; the water was allowed to cool, and this button of 18.64 grams was weighed in water and in air. As great care had been taken to remove all traces of silica and selenium, these two substances could not have affected the results. The greatest sources of errors are blow-holes, to which the extreme crystalline character of the metal makes it liable, the inclusion of oxide, and the presence of heavier metals. We have reason to believe that by our method of preparation these factors were avoided.

The specific gravity of antimony telluride is given by

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[1] Bull. Acad. Royal Belgique, **5**, 854.

[2] Bull. soc. chim., [2], **43**, 198.

[3] J. Am. Chem. Soc., **22**, 29.

[4] Chem. Centrbl., **2**, 962.

Bödeker and Giesecke as 6.47 to 6.51 at 13°. For the alloy containing 60 per cent of tellurium we obtained 6.46. The results for the other alloys were, as a whole, very unsatisfactory, and the values given in the following table are only approximate. Some of the alloys were so crystalline that it was impossible to obtain them free from air spaces. In certain cases large, drusy cavities were found in the center of an ingot after weighing. This tendency to form intercrystalline cavities was especially marked in the alloys containing from 0 to 40 per cent of tellurium. Beyond this point there was a tendency for the eutectic alloy to fill up these spaces, as is shown in Fig. V., where the eutectic has flowed in between the long, parallel crystals of antimony telluride. The crystals in this case are colored dark, on account of superficial oxidation, but ordinarily are almost silver-white.

Table II.—Specific Gravities of the Alloys of Antimony and Tellurium.

(Shown graphically in Fig. III.)

Weight of specimen. Grams.	Tellurium. Per cent.	Specific gravity.
18.6462	100	6.243
6.1011	90	6.264
0.703	80	6.56
0.941	80	[1] 6.17
3.681	80	6.370
6.201	70	6.370
5.4491	60	6.462
8.9995	50	6.347
3.8007	40	6.496
4.2680	30	6.615
7.7445	25	6.564
6.4322	20	6.601
2.5014	10	6.717
12.3573 (Pure antimony.)	0	6.693

As the percentage of tellurium approaches the amount necessary for the eutectic alloy, the structure is somewhat micaceous, some of the planes of fracture showing a matte surface. This micaceous structure is responsible for a turning over of edge, and is very evident when one attempts to pulverize a piece in a mortar. Most of the other alloys show a remarkable crystalline cleavage, the surfaces of which are very brilliant.

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[1] Three specimens from one ingot.

Both antimony and tellurium, and all their alloys, have approximately the same degree of hardness, somewhat above 2.5 (mica) and decidedly lower than 4 (fluorite). From 0 to 20 per cent of tellurium, the alloys closely resemble antimony.

Microscopical Examination of the Alloys.

The preparation of satisfactory samples for microscopic examination proved to be very difficult. On account of the highly crystalline character of some of the specimens, there was a great tendency for small fragments to split out along cleavage planes, thus leaving a pitted surface. By careful treatment a fairly satisfactory surface could be obtained by

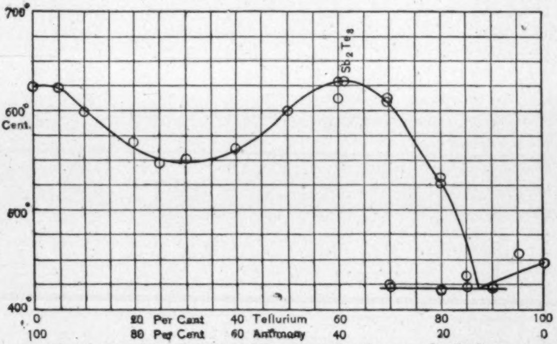

Fig. I.—Freezing-point curve of the alloys of antimony and tellurium.

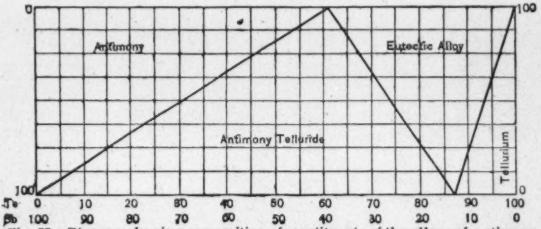

Fig. II.—Diagram showing composition of constituents of the alloys of antimony and tellurium.

first rubbing on an oil-stone under water, then polishing lightly on a wheel with a mixture of rouge and stearic acid, and finally on a piece of chamois stretched on a wooden block.

The process of etching was likewise difficult. Hydrochloric and nitric acids and iodine were all used without any appreciable effect. The best results were finally obtained by electrolysis in either dilute hydrochloric acid or ammonia. The specimen to be etched was attached to one of the poles of a battery and a current of about 0.1 ampere was allowed to pass for a few minutes. The structure was brought out by this means, but there was considerable superficial oxidation which produced beautiful colored effects on the surface. This darkening effect is well shown in Fig. V., where the crystals of Sb_2Te_3 have branched out through the eutectic alloy. Before etching, the whole surface was brilliantly white, but after etching, the crystals were colored a beautiful blue, which, in some cases, revealed the structure to the naked eye. The alloys from 0 to 60 per cent of tellurium were all richly colored, and showed under the microscope a uniform crystalline field with the single exception of the alloy containing 5 per cent of tellurium, which was composed of rounded granules of antimony telluride embedded in pure antimony. A cross section of any of these alloys showed branching crystals extending from the bottom to the top of the ingot.

The alloy containing 61.37 per cent of tellurium presented an absolutely uniform appearance, being composed entirely of the compound Sb_2Te_3, and is shown in Fig. IV. The dark spots in the photograph show the cavities produced as a result of the crystallization. With an increase in the percentage of tellurium beyond this point, the eutectic alloy of antimony telluride and tellurium began to show. In alloy No. 11, Fig. V., this is shown very clearly. In this alloy long crystallites of antimony telluride appear throughout the mass, and the space between the separate crystals is filled with the eutectic. In this case the crystals are dark on account of the superficial oxidation produced in etching.

Fig. VI. shows the appearance of the eutectic alloy, as it was usually found in the alloys containing from 60 to 90 per

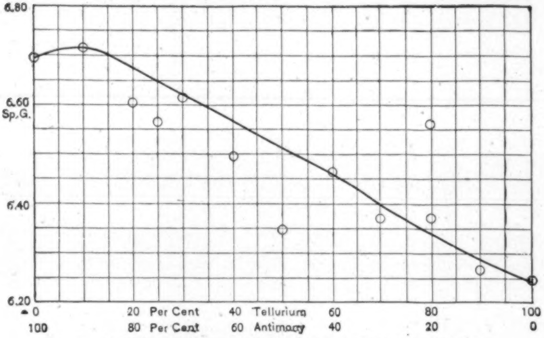

Fig. III.—Specific-gravity curve of the alloys of antimony and tellurium.

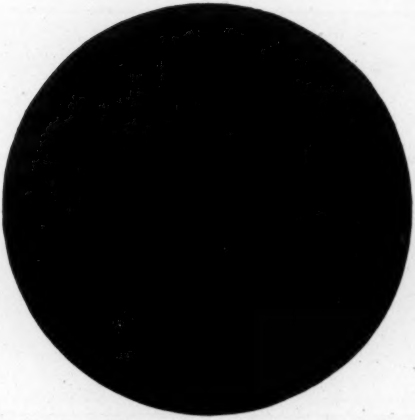

Fig. IV.—Alloy No. 9. The entire field consists of antimony telluride, Sb_2Te_3. (Magnified 95 diameters.)

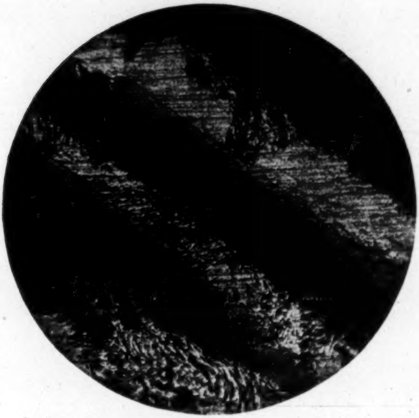

Fig. V.—Alloy No. 11. Dark, crystallites of antimony telluride ; light, eutectic of antimony telluride and tellurium. (Magnified 95 diameters.)

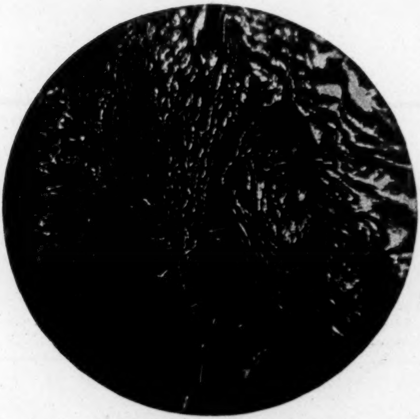

Fig. VI.—Eutectic alloy. Slowly cooled ; etched with hydrochloric acid. (Magnified 95 diameters.)

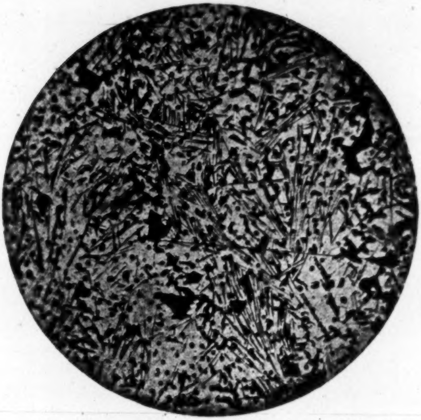

Fig. VII.—Eutectic alloy. Cast on porcelain; unetched. (Magnified 95 diameters.)

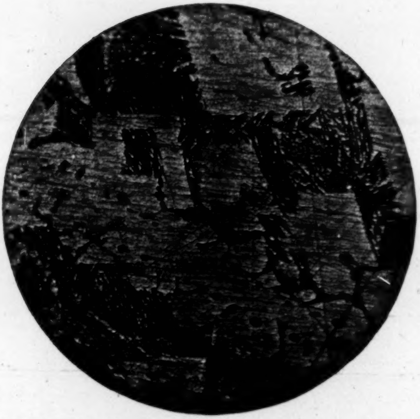

Fig. VIII.—Alloy No. 15. Light, pure tellurium; dark, eutectic of tellurium and antimony telluride. (Magnified 95 diameters.)

cent of tellurium. In slowly cooled alloys the structure was invariably the same, but more rapid cooling produced an entirely different appearance. Fig. VII. represents a photograph of the pure eutectic, prepared from several other alloys by pouring off the still liquid mass after a part had solidified. The photograph represents a surface which had been cast on glazed porcelain, and was taken just as it appeared after cooling, without any further treatment. The light background is tellurium, and the dark portions are antimony telluride. The latter was probably brought out in such great contrast on account of its extreme tendency to oxidize.

Fig. VIII. shows the usual appearance of the alloys consisting of the eutectic and an excess of tellurium.

It is proposed to study in the same manner other binary alloys of tellurium, and subsequently some of the ternary alloys.

Contributions from the Sheffield Laboratory of Yale University.

XC.—ELECTRO-AFFINITY AS A BASIS FOR THE SYSTEMATIZATION OF INORGANIC COMPOUNDS.

BY JAMES LOCKE.

In an article published a short time ago,[1] Abegg and Bodländer develop the conception "true electro-affinity," which they define as the strength of union between an ion and electron, or the intensity with which an ion holds its charge of positive or negative electricity. They then attempt to show that certain properties and reactions of inorganic salts are directly dependent upon the electro-affinities of the respective negative and positive ions. These properties are, especially, (1) solubility, and the tendency to form complex (2) positive, and (3) negative ions.

(1) *Solubility.*—The authors assert, as a general law, that the greater the electro-affinity of a positive or negative ion, the greater will be the solubility of its salts. The statement is modified, however, by the additional law, that when the electro-affinity of one of the ions is very great, and that of

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[1] Ztschr. anorg. Chem., 20, 453.

the other small, the influence of the first will overcome that of the second, and the salt of the two will be soluble. In conformity with these laws, salts yielding sodium ions, the electro-affinity of which is very great, are in almost every case soluble in water. Salts yielding silver ions, which have a very low electro-affinity, are, on the other hand, generally insoluble. But silver nitrate, inasmuch as the electro-affinity of the NO_3^- ion is exceptionally high, dissolves readily. In cases, however, in which the electro-affinity of both the positive and negative ions is high, the reverse order seems to be followed, and the salts become in such cases less soluble than when the value for only one of the ions is great. That this would necessarily be so is indicated in the fact that for ions of very small electro-affinity the influence of the latter upon the solubility increases more rapidly than do the electro-affinities themselves. As an approximate measure of the electro-affinities, we may take the decomposition voltage of the salts. The effect of change in electro-affinity may then be seen in a comparison of the decomposition voltage values for zinc and silver. For silver, in volts, it is -0.78 ($H = 0$), for zinc it is $+0.74$. The increase of 1.52 volts, in passing from silver to zinc, increases the solubility of the chlorides by the million-fold. The decomposition voltage of sodium is about $+2.8$, and at the same rate of progression, therefore, the solubility of sodium chloride would be something like 10,000,000 gram-molecules per liter. Since work can be gained on the dissolving of a salt in water, a salt of such solubility would have too great a supply of energy to be stable at all. The authors assume, therefore, that it passes into a modification with far less energy, which, accordingly, does not admit of comparison with the zinc and silver salts. This is an exceedingly important hypothesis, without which the theory could not stand for an instant.

(2) *Formation of Complex Ions.*—Abegg and Bodländer define a complex compound—metallo-amines, double salts, etc.—as follows:

Complex compounds are those in which one of the ionogenic constituents is made up of a single ion capable of independent existence (single ion), coupled with an electrically neutral molecule (neutral component).

Thus, potassium ferricyanide has as its ionogenic constituents potassium and the negative complex $Fe(CN)_6^{---}$, which is composed of the single-ion CN^- and the neutral component $Fe(CN)_5$. No distinction is made between compounds which break down into their molecular constituents in solution, such as the salt $KMgCl_3$, and salts, the complex ions of which are stable in solution, *e. g.*, potassium ferrocyanide, $K_4Fe(CN)_6$.

The greater the tendency to ionization, which may be shown by the neutral component, the more loosely, as a natural sequence, will the complex be held together. The greatest tendency to form ionic complexes, therefore, is to be expected in those cases in which the neutral component, if a salt, is one in which both the ionogenic constituents have low electro-affinities. Only very few double salts are known which contain salts of the alkali metals as their neutral components, and such as have been observed (*e. g.*, $KNaCO_3$) are, at least, of extreme instability. On the other hand, the double salts of silver, gold, etc., the electro-affinities of which metals are very low, are plentiful, and marked, in many cases, by the almost total absence of dissociation of their complex ions in solution.

The tendency to the formation of complex ions is also influenced by the nature of the single-ion. Since the product of the electrolysis of complex compounds is almost invariably the single-ion, not the complex, it follows that the electro-affinity of the complex is greater than that of the single-ion. In other words, *the electro-affinity of the single-ion is increased by its union with the neutral component.* Inasmuch, therefore, as in the presence of a strong opposite ion a weak ion is compelled to ionization, it seeks to *strengthen* itself by combination with a neutral component.

This portion of the authors' theory is widely extended to include not only double salts, metallo-amines, hydrated salts, and the like, but also the formation of poly-acids (*e.g.*, $K_2Cr_2O_7 = K_2^+, {}^+CrO_4(CrO_3)^{--}$), and even oxy-acids in general. The chlorate ion, ClO_3^-, for instance, is regarded as a complex with a single-ion Cl^- and the neutral component $3O$. To these extensions of the theory I will return at a later point.

The properties of the sodium salts may be briefly summarized as follows :

(1) Solubility in water.

(2) Non-entrance into the negative complexes of double salts.

(3) Non-entrance into complex cations, such as metallo-amines.

(4) Stability on ignition, or passage thereon into another salt, never into the oxide.

These collective properties apply to almost every sodium salt known, and by their application the behavior of each single salt is roughly described. For instance, since sodium does not enter into complex anions, its chloride is less soluble in hydrochloric acid than in water. Potassium salts, like those of sodium, are soluble in water; and since, in showing this one property, they exhibit in about the same degree all the others common to the sodium compounds, it must be concluded that these properties are not independent of one another, but correlated and due to one and the same ultimate cause. The same is true of the silver and cuprous compounds. In so far as they are capable of existence, the cuprous compounds, in exhibiting a single generic property common to silver compounds, conform to the latter in all their generic reactions, exclusive of those of oxidation.

Any theory which brings to the front a cause to which these properties may be due, must be of the greatest service to the science. This the theory of Abegg and Bodländer in part attempts, for it refers each of the properties enumerated, indirectly that of stability on ignition as well as the others, to the approximately equal values of the electro-affinities of the metals in the sodium group and silver group respectively. But as a direct sequence of the theory these properties should always go hand in hand with one another. Exceptions in regard to the solubilities of a few individual salts can be explained as the authors have explained the relative solubility of sodium chloride and zinc chloride. But any instance in which one generic property of, let us say, silver salts is shown *in extenso* by the compounds of a metal, when they have not the remaining generic properties of silver salts, must be regarded only as a flat contradiction of the theory, and render its admissibility at least very doubtful. This is especially true in a case in which the electro-affinity of the metal approximates that of silver.

The electro-affinity of thallous thallium is very small, and this fact is used by the authors to explain the slight solubility of thallous halides. In addition to the iodide, the sulphide, chromate, dichromate, sulphocyanate, vanadate, hypophosphate, ferrocyanide, and other compounds are practically insoluble in water. These are also the most difficultly soluble silver salts. The sulphite, thiosulphate, triorthophosphate, chloride, bromide, and many others, dissolve only slightly. The solubility, in general, is somewhat greater than that of silver salts, but less than that of zinc and cadmium compounds; and thallium, in accordance herewith, has a much lower electro-affinity than have these metals. Now both zinc and cadmium yield double salts in which they form part of the neutral components. They form metallo-amines—complex positive ions—in great plenty and of much stability. How much more readily, therefore, should such salts be formed by thallium, which, in the matter of electro-affinity, is nearer silver, and which, like the latter metals, forms sparingly soluble salts. Not a single metallo-amine of thallous thallium has ever been prepared. Thallous chloride is far less soluble in chloride solutions,[1] the iodide in iodide solutions, than in water. Were it not for a complex thiosulphate and sulphocyanate, we might justly say that the power of thallium to enter into double salts is absolutely *nil.* A double salt of thallium with one of the weakest anions, S^{--}, cannot be obtained even in the dry way.

We have here, therefore, two of the three generic properties of salts of a metal with low electro-affinity almost entirely absent—the formation of complex cations and complex anions—while the third, sparing solubility, is present in full force. Nor is this the only refractory case. There are almost as many others as there are elements, and one or two of these I may touch upon briefly. It will be seen that while the salts of metals of the same valence can almost always be divided into groups according to their generic properties, as above, we do not necessarily find the same properties in correlation. A tendency to double salt formation does not in the least necessitate a tendency to form complex cations; nor does general slight solubility in water necessitate the formation of either anions or cations of complex nature.[1]

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[1] Noyes: Ztschr. phys. Chem., 9, 606.

Dividing the metals into groups according to their valence, the authors state that their electro-affinities lie, in general, in the same order as the positions of the elements in the periodic system. In the different families the electro-affinities increase with increasing atomic weight. The series Cu^I, Ag, Au^I, and Zn, Cd, Hg^{II}, follow the reverse order. While "direct measurements are in most cases wanting, this arrangement is obvious from the solubilities, strength of acids, and general chemical behavior." As has been stated, the electro-affinities may be roughly measured by the decomposition voltage of the metals. To show the relative magnitudes I include some of these values in the following table:

Li	Be	N	F
Na(+2.8?)	Mg(+1.47)	P	Cl(+1.31)
K	Ca	As	Br(+0.94)
Rb	Sr	Sb(—0.13)	I(+0.52)
Cs	Ba		

Au	Hg
Ag(—0.78)	Cd(+0.38)
Cu	Zn

Furthermore, for members of the eighth family, we have:

Mn(+1.06) Fe^{II} +0.33   Ni +0.22   Co +0.22

The decomposition voltage of the alkaline earth metals has not been determined, but it is undoubtedly higher than that of magnesium, and less than that of sodium.

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[1] That the electro-affinity theory requires this correlation, nevertheless, is shown by Abegg and Bodländer themselves. The instance of platinic platinum is cited as an exception in that while yielding double salts in abundance it forms metallo-amines with difficulty. They explain this by the assumption that the platinic ion is so weak that it can hardly exist even when strengthened by the addition of NH_3 molecules. This difficulty, however, may easily be overcome by considering only cases in which the metallic ions are easily capable of independent existence—*e. g.*, Ba+ +, Zn+ +, etc.

Now let us compare the solubilities of the barium salts with those of sodium on the one extreme and of zinc on the other. The statement of Abegg and Bodländer, that when both cation and anion possess very great electro-affinities the salt is apt to pass into a form unsuitable for comparison, should apply to barium salts in a less degree than to those of sodium, since the electro-affinity of barium is less than that of sodium. But to avoid confusion arising from this source, the following list has been made up mainly of salts of weak anions:

	Sodium.	Barium.	Zinc.
Nitrate	Sol.	>Sol.<	Sol.
Chloride	"	>Sol.<	"
Fluoride	"	Insol.	Slightly sol.
Sulphate	"	"	Sol.
Chromate	"	"	"
Selenate	"	"	"
Thiosulphate	"	>Slightly sol.<	"
Hypophosphite	"	>Insol.	"
Iodate	"	"	"
Phosphite	"	"	"
Silicofluoride	"	"	"
Sulphite	"	>Slightly sol.<	"
Dithionate	"	>Sol.<	"
Nitrite	"	"	"
Hyponitrile	"	Insol.	. .
Oxalate	"	"	Sol.
Carbonate	"	"	Insol.
Phosphate	"	"	"
Cyanide	"	Slightly sol.	"

Among the salts of other acids there are a few, such as the arsenates, of which both the barium and zinc salts are insoluble; in the majority of cases, however, no data can be obtained for comparison. But from this list alone it can readily be seen that the barium salts are, in general, insoluble or sparingly soluble, that the corresponding zinc salts are usually soluble. As a rule, furthermore, the solubilities of the calcium salts approximate those of barium, though somewhat higher (in spite of the fact that the electro-affinity of calcium is less). But neither of these metals, though their salts are sparingly soluble, show in more than the slightest extent a tendency to enter into complex ions. The only double salt of barium with a monobasic acid, mentioned in Dammer, is the compound $K_2Ba(NO_2)_4$. Ammonia addition-products can be obtained only in the dry way, and these break down completely into salt and ammonia in presence of water.

The solubilities of the salts of magnesium, manganese, ferrous iron, nickel, cobalt, copper, and cadmium are qualitatively almost exactly the same as those of zinc compounds, though in the matter of decomposition voltage the metals range from + 1.47 to + 0.22. Here, in the matter of solubility, we have quantitative data which can be compared directly with the electro-affinities, or with the decomposition voltage values, which roughly measure the latter. The solubilities of the nitrates, $M(NO_3)_2.6H_2O$, at 18°, expressed in gram-molecules per liter of solvent, are as follows :[1]

	Mg.	Mn.	Fe.	Co.	Ni.	Cu.	Zn.	Cd.
Solubilities	4.95	7.41	4.57	5.40	5.12	6.13	6.08	5.37
Voltage	+1.47	+1.06	+0.33	+0.22	+0.22	—0.34	+0.74	+0.38

There can be no question here as to whether a relation exists between solubility and decomposition voltage. Magnesium nitrate, instead of being the most soluble, is, with one exception, the least so. Cupric nitrate is the most soluble, with one exception, and copper has by far the lowest decomposition voltage and electro-affinity.

I have determined the solubilities of the isomorphous double sulphates of the formula $M_2^{I}M^{II}(SO_4)_2.6H_2O$ with similar contradictory results. Not only is the order different from that of the decomposition voltage values, but from that of the nitrate solubilities as well. For the ammonium salts, at 25°, the solubilities are as follows :

Mg.	Mn.	Fe.	Ni.	Co.	Cu.	Zn.	Cd.
0.791	1.321	....	0.261	0.500	0.778	0.480	2.125
+1.47	+1.06	+0.33	+0.22	+0.22	—0.34	+0.74	+0.38

For the discussion of these figures, suffice it to point out that the solubility of the nickel salt is one-third that of the magnesium compound, while the difference between the decomposition voltages of the two metals is about the same as that which causes the difference in solubility of zinc chloride and silver chloride (see above, where the statements are a more or less literal translation of the author's words); and that although the copper salt, by analogy, should be about as soluble as silver chloride, it too is three times as soluble as the nickel salt.

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[1] Funk : Ztschr. anorg. Chem., 20, 393, f.f.

In spite of the fact that the salts of these metals are, in general, more soluble in water than those of the alkaline earths, and the latter enter into no complex ions, we have in this group stable or unstable complex ions of either positive or negative nature. The double cyanides of all except magnesium are in fact very stable indeed. Double chlorides, bromides, iodides, exist in great abundance. Stable complex amines are known of all the heavier metals of the group, and in concentrated ammoniacal solution magnesium probably forms them to a marked extent as well.[1] These metallo-amines, however, show, like the double salts, no gradation in accordance with electro-affinities, a fact observed and commented upon by Dawson and McCrae.[2] These investigators found from measurements of distribution constants on ammoniacal solutions containing salts of nickel, copper, zinc, and cadmium, that the tendency to form complex ions is about the same for all, although the decomposition voltage of the metals ranges from $+0.22$ to $+0.74$.

The thallous salts, as has been seen, show the sparing solubility which is in conformity with the low electro-affinity of thallium, while in other respects they approach the salts of the alkali metals, and have properties exactly the reverse of those which we would expect. The zinc salts, on the other hand, although the electro-affinity of zinc is likewise low, are mostly very soluble; but then they conform to its magnitude in yielding both positive and negative complex ions. To touch briefly upon the trivalent metals, the salts of aluminium and iron with weak acids, so far as they have been obtained, are, as a rule, insoluble bodies. They also form double salts with readiness, in conformity with the low electro-affinities of the metals. But no positive complex ions of these metals are known. Ammonia simply precipitates the hydroxides. There may be a few cases in which the three properties called for by the theory go hand in hand, and these Abegg and Bodländer have sought out and used with great dexterity. But inorganic chemistry is not the chemistry of sodium and silver alone.

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[1] Unpublished experiments of the author.

[2] Ztschr. anorg. Chem., **26**, 99.

Double Salt Formation.—For the purpose of discussion, we may divide double salts into three classes :[1]

A. Salts, the complex ions of which are not appreciably decomposed in solution.

B. Salts, the negative ions of which dissociate to a very marked extent, but which are obtained by crystallization from solutions containing equivalent quantities of their molecular constituents.

C. Salts almost completely dissociated, like the last, but which form only when one of their constituents is present in excess.

According to the view of Abegg and Bodländer, the weaker the anion of a double salt is, the more readily will it seek to *strengthen itself by the addition of a neutral component*. Referring for the moment only to the double salts, the single ions of which are univalent, we see that in the compounds of class *A* this seems to be true. The most frequent double salts of this class are the complex cyanides, the neutral components of which are insoluble in water. This latter fact is in accord with that part of their theory which states that *the stronger the anion is the more soluble will be the salt*. But the authors seem to have absolutely lost sight of this feature of their theory in its application to the unstable double salts of class *B*, the existence of every member of which is in direct contradiction to it. If the anion of a chloride is strengthened by the addition to it of a neutral chloride, then the resulting double salt should be more soluble than the simple chloride itself. Professor H. L. Wells, and his co-workers in this laboratory, have found, in long investigations of double caesium halides, that hardly a single such salt, if any at all, is more soluble than caesium chloride alone. I have found that in the case of the alums,[2] where the electro-affinity of the

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[1] Wells: This JOURNAL, **26**, 389.

[2] *Ibid.*, **26**, 166.

SO_4^{--} ion is strengthened by the addition of the neutral component $M_2^{II}(SO_4)_3$ (A and B, p. 472 f.f.), the fall in solubility from the potassium to the rubidium, and finally to the caesium, salts is enormous. In gram-molecules per liter the solubilities of the chromium alums at 25° are as follows:

K	0.441
NH_4	0.407
Tl	0.212
Rb	0.078
Cs	0.015

Two objections may be offered to this from the standpoint of the theory. First, in that when cation and anion are very strong, the salt will tend to be more sparingly soluble. Secondly, in that, as Abegg and Bodländer state, solubility at a definite temperature does not necessarily afford a suitable means of comparison. In answer to the first, we find that hardly a single simple potassium salt exists, which is more soluble than the corresponding caesium salt—in other words, that the fact of potassium salts being less soluble than those of sodium (owing to the greater electro-affinity of potassium over that of sodium, the salts of which show decreased solubility (A and B, p. 462), is absolutely no proof of this hypothesis. For caesium has, according to their own words, a higher electro-affinity than potassium. As regards the comparison at a given temperature, secondly, the justness of this comparison is proved by the fact that at the same temperature the solubilities of all the alums stand in definite mathematical relation to one another.[1]

A simple application of the law of solubility products will show at once not only that the solubility of an unstable double salt of class *B* must necessarily be less than that of its constituents, but that the absolute solubility of such compounds is in reality very small indeed. It has been shown again and again that in the equilibrium equation of a solution containing potassium sulphate and aluminium sulphate,

$$a_{K_2SO_4}\, b_{Al_2(SO_4)_3} = K\, c_{K_2Al_2(SO_3)_4}.$$

The dissociation constant K is very large. The high value of the solubility-product is, therefore, due entirely to this fact, and the solubility of the undissociated alum correspondingly small.

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[1] This JOURNAL, 26, 332.

The same conclusion must be reached if we regard the double salt as resulting from the preliminary formation of its complex ions; for the concentration of the latter, and therefore the solubility-product as well, must have, at least, an extremely low value.

But while the caesium double salts are probably in every case less soluble in water than the simple caesium salts, in contradiction to the theory, the relative solubilities of double salts of this metal, as compared with isomorphous compounds of the remaining alkali metals and ammonium and thallium, show no strict regularities. In the case of the double halides, it has generally been found that the solubilities decrease from potassium to caesium. But with double sulphates no definite order is retained throughout different salt series. This is illustrated, for instance, in a comparison of the alums and double sulphates of the type $M_2^INi(SO_4)_2.6H_2O$ at 25°.

$M^ICr(SO_4)_2.12H_2O$.		$M_2^INi(SO_4)_2.6H_2O$.	
K	0.441	Cs	0.495
NH_4	0.407	NH_4	0.261
Tl	0.212	K	0.210
Rb	0.078	Rb	0.143
Cs	0.015	Tl	0.070

There can be no thought here of a conformity to any one of the laws proposed by Abegg and Bodländer. The relatively great solubility of the thallium alums, in spite of the low electro-affinity of thallium, is opposed to them in the one instance; and in the other absolutely no suggestion of gradation according to the theory can be found.

The further extension of the theory is so indefinite and faulty that one can hardly tell where to begin, still more where to leave off, in criticizing it. The authors go beyond the definition of complex compounds cited above, in including among these the acid salts on the one hand and basic salts on the other. In these cases the neutral components are replaced by the ionogenic components, H^+ and $(OH)^-$. As an instance of the strengthened nature of the resulting complex ion, the increase in solubility of acid salts over neutral salt is cited; *e. g.*, barium acid sulphate, barium acid phosphate, barium acid carbonate, etc. The metallic ions, in analogy, must be *strengthened* by the addition of hydroxyl groups. Are basic salts, then, more soluble than the normal compounds? It is difficult to understand how any one who has ever partially neutralized a copper nitrate solution, or who has even ever seen a reasonably old solution of ferric chloride, can make such an assumption.

A great many compounds are cited, with reference to one property or another, by Abegg and Bodländer. At least as many as one-half their examples, if observed with reference to any other properties than those chosen, would be flatly contradictory to their views. For instance, the chlorate ion, ClO_3^-, is the chlorine ion, Cl^-, strengthened by oxygen as a neutral component. Many chlorates are, therefore, more soluble than the chlorides. The periodate ion is the iodine ion strengthened in the same manner. Periodates must, therefore, be more soluble than iodides! The very weak ion Hg^{++} strengthens itself by the addition of another Hg, thus forming the much stronger mercurous ion $(Hg.Hg)^{++}$. Are then the mercurous salts more soluble than the mercuric?

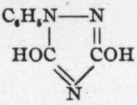
The physical chemist is not the only one who regrets the more or less tardy acceptance of the newer theories by the teachers of inorganic subjects. There are many of us whose line of study lies wholly in inorganic fields, who are willing and anxious to do such missionary work as we can for the extension of those theories. But the publication of such speculations as the above, by men prominent in the physico-chemical world, does not materially assist toward that end, for it naturally raises doubts as to the accuracy and range of our colleagues' knowledge of practical chemistry. It is as a protest in the name of that practical, experimental chemistry, that the above criticisms are submitted.

NEW HAVEN, December, 1901.

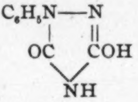
CONSTITUTION OF PHENYLURAZOLE (I.)

By S. F. Acree.

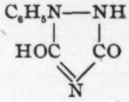
Phenylurazole was first made by Pinner,[1] and several derivatives have been described since then, but the constitution of none of these compounds has been determined. Various formulas have been suggested for phenylurazole itself, and it must have one of the following :



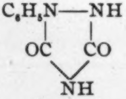
I.



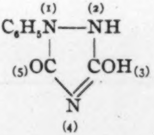
II.



III.



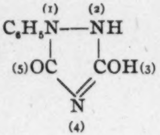
IV.



V.

It will be shown that formula V. is the only one that harmonizes with the results obtained.

In designating the position of the groups attached to the urazole ring we shall make use of the system now in vogue, numbering the five atoms in the ring, as follows :



A substance with this formula has the name 1-phenyl-2-hydro-3-hydroxy-5-oxyurazole. A substance with the formula

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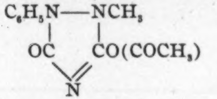
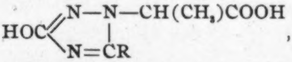
[1] Pinner : Ber. d. chem. Ges., 20, 2360 ; 21, 1220.



has the name 1-phenyl-2-methyl-3-oxyacetylurazole.

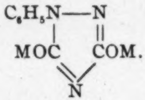
It was shown by Bailey and Acree[1] that triazole derivatives of propionic acid,



are strong dibasic acids giving a sharp reaction with two molecules of sodium hydrate, using phenolphthaleïn as the indicator, that is, the triazole group,

$$—NHCO— \rightleftarrows —N{=}C(OH)—,$$

is a strongly acid group forming neutral sodium and silver salts, —N=C(OM)—. If phenylurazole had the formula I., II., or III., it should form a neutral disodium (or disilver) salt with the formula



But phenylurazole is a monobasic acid, giving a sharp reaction with one molecule of sodium hydrate and giving only a monosilver salt. Although the disodium salt can be formed by boiling phenylurazole with sodium alcoholate, in absolute alcohol, yet it gives a strongly alkaline reaction when dissolved in water, indicating that one of the sodium atoms of the salt is joined to a nitrogen atom of the urazole ring.[2] Phenylurazole must then have the formula IV. or V. Since it gives a violet color with ferric chloride in alcohol solution just as phenol, acetoacetic ether, and triazoles[3] do, it is very likely that the substance has an enol group, —N=COH—.

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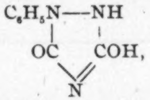
[1] Bailey and Acree: Ber. d. chem. Ges., **33**, 1520.

[2] Thiele and Schleussner: Ann. Chem. (Liebig). **295**, 171.

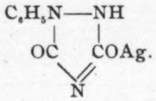
[3] Bailey and Acree: Ber. d. chem. Ges., **33**, 1520.

Hence formula IV. is excluded, and phenylurazole has the formula V.,

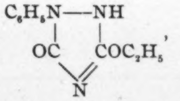


or is 1-phenyl-2-hydro-3-hydroxy-5-oxyurazole.

The silver salt, beyond question, has the formula



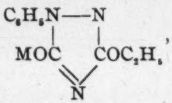
When treated with ethyl iodide in absolute ether in the cold, it gives the 1-phenyl-2-hydro-3-ethoxy-5-oxyurazole,



insoluble in alkalies. The imide =NH group of a urazole or triazole ring is not acid enough, or does not give enough hydrogen ions, to form neutral salts in a water solution. The neutral salts of these urazoles have the metal combined with oxygen, forming the group —N=C(OM)—, and only when we have an imide group next to a carbonyl group as

$$\text{—NH—CO—} \rightleftarrows \text{—N=C(OH)—}$$

can we have these neutral salts formed. Wheeler[1] has made the isomeric compound with the ethoxy group at 3, and it is soluble in alkalies, as we should expect, forming the salts



and is precipitated by strong acids. When the isomeric

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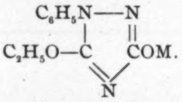
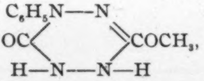
[1] Wheeler: J. Am. Chem. Soc., 1900, p. 377.

5-ethoxy compound is made it will doubtless have acid properties, forming the salts

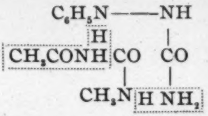


When the sodium or silver salt of phenylurazole is treated with methyl iodide in alcohol at 100° C. a N-methyl derivative having the melting-point 183° to 185° is formed, which is not affected by evaporating with concentrated hydrochloric acid. This compound is doubtless identical with the methylphenylurazole, melting at 183° to 185°, made by Busch and Heinrichs;[1] by the action of nitrous acid on 1-phenyl-2-methyl-3,5-oxy-4-aminourazole. These writers ascribed the isomeric urazine formula,



to this amino body, but this is clearly wrong, for two reasons. First, such a urazine should be soluble in alkalies, while their compound was insoluble; this we should expect if it had the above urazole formula. Secondly, it could not be a methoxy derivative, for both their so-called "urazine" and the phenylmethylurazole made from it are very stable towards acids (hydrochloric acid).

The isomeric 1-phenyl-4-methylurazole was made by a method which could not give the 2-methyl compound. When phenylsemicarbazide is heated with methylacetylurea to 200° C. the reaction may be represented by the following:



This compound melts at 225° and is stable toward concentrated hydrochloric acid at 100°. So phenylurazole, upon alkylation by means of potassium hydroxide and methyl iodide, gives 2-alkyl derivatives, and we shall use this method to prepare other homologues.

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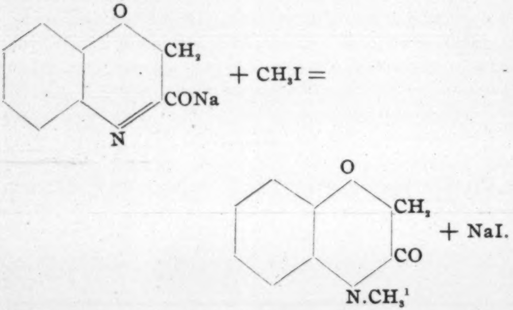
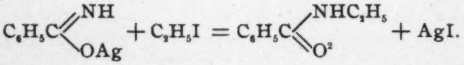
[1] Busch and Heinrichs: Ber. d. chem. Ges., 33, 455.

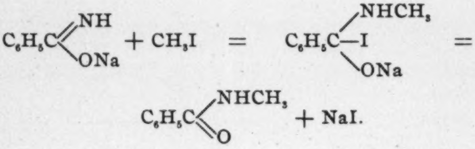
It might be thought surprising that in the alkylation of phenylurazole by potassium hydroxide and methyl iodide no methylation takes place at 4.





$$C_6H_5C\begin{cases}{=}NH\\ {-}OAg\end{cases} + C_2H_5I = C_6H_5C\begin{cases}{-}NHC_2H_5\\ {=}O\text{[2]}\end{cases} + AgI.$$

Here we have alkylation on the nitrogen which is doubly linked to the $=\underset{\diagdown}{C}OM$ group, and this reaction was formerly[3] thought to depend upon the addition of methyl iodide to the double bond and a subsequent loss of sodium iodide :



$$C_6H_5C\begin{cases}{=}NH\\ {-}ONa\end{cases} + CH_3I = C_6H_5C\begin{cases}{-}NHCH_3\\ {-}I\\ {-}ONa\end{cases} = C_6H_5C\begin{cases}{-}NHCH_3\\ {=}O\end{cases} + NaI.$$

Nef[4] has recently shown that in all cases of methylation by means of methyl iodide there is first a dissociation into methylene, $CH_2=$, and hydriodic acid. The hydriodic acid may displace the metal and the methylene acts at the most favorable position, which, in the case of phenylurazole, happens to be at 2. Furthermore, if phenylurazole has the formula V., since there is no hydrogen at 4, we cannot have methylation at that place unless we assume the addition of water or hydriodic acid to the double bond between 3 and 4. Another similar case occurs in the methylation of 3-methyl-2,6-oxy-7-hydro-8-chlorpurine (3-methylchlorxanthine), which yields 8-chlortheobromine, and of 3-methyl-2,6-oxy-7-hydropurine (3-methylxanthine), which yields theobromine.[1]

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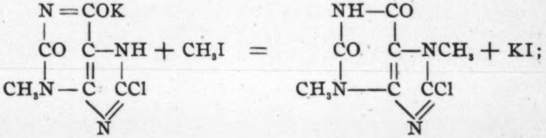
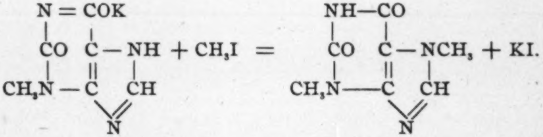
[1] Wheeler : This Journal, **20**, 560.

[2] Wheeler : *Ibid.*, **21**, 185.

[3] Nef : Ann. Chem. (Liebig), **266**, 62 ; **280**, 287.

[4] Nef : *Ibid.*, **309**, 126.





The methylation takes place at 7 and not at all at 1; hence the reaction cannot depend upon the addition of methyl iodide to the double bond between 1 and 6, and Nef's explanation seems to clear up the reaction.

If the above formula for phenylurazole be correct, we should expect two series of acyl derivatives—N- and O-acyl derivatives. The N-derivatives are acid amides and are comparatively stable. But the oxyacyl derivatives are really acid anhydrides, and we should expect them to be readily hydrolyzed by alcohol and water. This I have found to be the case. When the silver salt of phenylurazole is treated with acetyl chloride in benzene solution in the cold, a reaction slowly takes place and the odor of acetyl chloride disappears.

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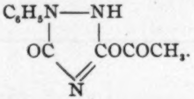
[1] E. Fischer and Ach: Ber. d. chem. Ges., 31, 1980.

From the benzene solution there is obtained an oil having the constitution



This, on boiling with alcohol a few minutes, or on standing in water solution, gives pure phenylurazole, melting at 264°. The isomeric 2-acetylphenylurazole is formed by the action of acetic anhydride on phenylurazole and is purified by crystallization from water and alcohol, and the neutral 2,3-diacetyl-1-phenylurazole is so sensitive to the action of water that it must be crystallized from some solvent like benzene. When crystallized from hot water it loses the O-acetyl group at 3 to give the acid 2-N-acetyl-1-phenylurazole.[1] This is a fine example, showing how much more stable the N-acyltriazoles, urazoles, etc., are than the O-derivatives. Bailey and Acree[2] showed that most of the 3-hydroxy-5-alkyltriazole-1-propionic acids have the enol structure. With diazomethane they give methoxytriazoles, which give methyl chloride when treated with concentrated hydrochloric acid. Hence we should expect their O-acetyl and benzoyl derivatives to be readily hydrolyzed by hot water, and this is indeed the case. When the 3-oxyacetyl-5-styryltriazole-1-propionic acid, melting at 168°, or ethyl 3-oxyacetyl-5-phenyltriazole-1-propionate, which melts at 80°, is boiled one hour with 75 per cent alcohol and the solution is cooled, there is obtained a precipitate of the pure 3-hydroxy-5-styryltriazole-1-propionic acid, which melts at 243°, or ethyl 3-hydroxy-5-phenyltriazole-1-propionate, which melts at 172°, respectively, showing that there is complete hydrolysis of these acyl derivatives.

Rupe and Labhardt[3] found that 1-phenyl-5-oxyacetyltriazole by evaporation with alcohol loses the acetyl group and gives the 1-phenyl-5-oxytriazole,

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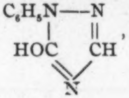
[1] Thiele and Schluessner: Ann. Chem. (Liebig), 295, 171.

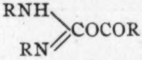
[2] Bailey and Acree: Ber. d. chem. Ges., 33, 1520.

[3] Rupe and Labhardt: Ber. d. chem. Ges., 33, 233.



which melts at 178° to 181°; without doubt the acetyl was joined to the oxygen at 5.

Dains[1] attempted to prepare isoacylureas of the type

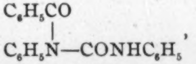


$$\left.\begin{matrix}\mathrm{RNH}\\ \mathrm{RN}\end{matrix}\right\rangle\mathrm{COCOR}$$

by the addition of acetic acid, etc., to *o*-carboditolylimide. Instead, the product of hydrolysis, *o*-carbtoluide,

$$(C_7H_7NH)_2CO,$$

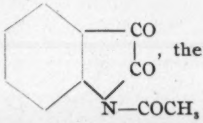
was obtained, as the intermediate isoacylurea is too easily hydrolyzed. N-benzoyldiphenylurea,

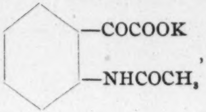


$$\begin{matrix}C_6H_5CO\\ |\\ C_6H_5N\text{—}CONHC_6H_5\end{matrix},$$

on the other hand, is very stable toward alcohol and water.

Dr. J. H. Ransom,[2] of Purdue University, writes me that when he boiled N-benzoylcarbonyl-*o*-aminophenol for one hour with water, the unchanged body, which melts at 174°, was recovered.

In acetylisatin,  , the acetyl is so firmly bound to the nitrogen that it gives acetylisatinic acid,[3]



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[1] Dains: J. Am. Chem. Soc., **21**, 136.

[2] Ransom: This JOURNAL, **23**, 20.

[3] Baeyer and Oekonomides: Ber. d. chem. Ges., **15**, 2100.

when treated with potassium hydroxide solution. 1-Benzoyl-α-pyridone, when boiled with hydrochloric acid, gives

$$C_6H_5CONHCH = CH—CH{=}CHCOOH.$$

From these facts it is evident that the N-acyl derivatives of urazoles, triazoles, etc., or any compounds with the group

$$—CO—NH— \rightleftarrows —N{=}C(OH)—$$

are much more stable than the O-acyl derivatives, the latter being readily hydrolyzed by alcohol or water, as most other acid anhydrides are.

The phenylurazole used for this work was prepared by the action of alkalies on the dicarbethoxyphenylsemicarbazide, which substance was obtained directly in two modifications. One modification has the melting-point 172°; the other, the melting-point 154°. When the product melting at 172° is recrystallized from water several times the melting-point is lowered to 154°, and this form, when cooled, melts again at 172°. A sample of this product melting at 154° was mixed with a sample of the product melting at 154° which was obtained directly, but there was no change in the melting-point. Whether we have here the enol and keto tautomerism described by Claisen,[1] Wislicenus,[2] Gutzeit,[3] Bailey and Acree,[4] and others, must be decided by further work.

Work is now being carried forward on urazole- and thiourazole-1-propionic acids with Dr. J. R. Bailey, of Texas, and on 1-phenyl-3,5-dithiourazoles and 1-phenyl-3(or 5)-thio-5 (or 3)-oxyurazoles in this laboratory. We shall especially investigate the molecular conductivities of these compounds and their salts. We ask that this work be left to us.

EXPERIMENTAL.

Phenylsemicarbazide.—This substance was prepared according to Widman's[5] method. To 20 grams phenylhydrazine and 15 grams acetic acid in 250 cc. water kept at —5° was added the theoretical amount of potassium cyanate in a small amount of cold water. The phenylsemicarbazide precipitates out immediately, and upon recrystallization from alcohol has the melting-point 172°. Yield, 23.5 grams.

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[1] Claisen: Ann. Chem. (Liebig), **277**, 188; **291**, 25.

[2] Wislicenus: *Ibid.*, **291**, 147.

[3] Gutzeit: Ber. d. chem. Ges., **26**, 2795; Ann. Chem. (Liebig), **285**, 35, 61, 108.

[4] Bailey and Acree: Ber. d. chem. Ges., **33**, 1520.

[5] Widman: *Ibid.*, **26**, 2613.

Dicarbethoxyphenylsemicarbazide.—This substance was made by boiling 5 grams phenylsemicarbazide with 3.5 grams chlorcarbonic ether in 50 cc. acetic ether for four hours, with a return condenser. Upon cooling, the substance precipitates out as a white solid, melting undecomposed, at 172°. When mixed with a sample of phenylsemicarbazide, melting at 172°, the melting-point was lowered to 140°–150°. When recrystallized from water several times it had the melting-point 154°, and when solidified it melted again at 172°. One sample of this dicarbethoxy compound, made as above, failed to precipitate from the acetic ether till this was evaporated. The compound then had the melting-point 154°, and when mixed with the product melting at 154° obtained by recrystallization from water, the melting-point was not changed. Whether we are dealing here with tautomeric enol and keto forms or with physical modifications of the same substance, as in the case of benzophenone,[1] must be decided by further work.

Analysis:

I. 0.2780 gram substance (m. p. 172°), gave 0.5370 gram CO_2 and 0.1490 gram H_2O.

II. 0.2395 gram substance (m. p. 154°), gave 0.4608 gram CO_2 and 0.01274 gram H_2O.

	Calculated for $C_{13}H_{17}N_3O_5$.	Found.	
		I.	II.
C	52.83	52.37	52.37
H	5.82	5.95	5.87

Phenylurazole. — When this dicarbethoxy compound is heated with alkalies it gives phenylurazole. Eight grams of the ester heated four hours at 100° with an excess of caustic soda, when cooled and acidified, gave 4.5 grams phenylurazole, melting with decomposition at 264°. If the ester is treated only a short time in the cold with caustic soda and then acidified, no precipitate is formed. The phenylurazole is difficultly soluble in cold water and ether, but readily soluble in hot alcohol. With an alcoholic solution of ferric chloride it gives a dirty violet color, which proves the presence of an enol group. It is a strong monobasic acid, giving a sharp reaction with one molecule of caustic potash, using phenolphthaleïn and forming mono-silver and barium salts.

---

[1] Zincke: Ann. Chem. (Liebig), **159**, 377; R. Meyer: Ber. d. chem. Ges., **22**, 550.

0.2316 gram phenylurazole required 9.08 cc N/7 caustic soda instead of the calculated 9.15 cc.

Silver Salt.—This is made by adding the calculated amount of silver nitrate to the neutral sodium salt and boiling the solution. The precipitate is then easily filtered. It is very stable toward light, is easily soluble in ammonium hydrate, but insoluble in dilute nitric acid. It melts at 252° with decomposition, giving off fumes having a strong isocyanate odor.

0.2143 gram silver salt gave 0.0816 gram silver.

	Calculated for $C_8H_6N_3O_2Ag$.	Found.
Ag	37.90	38.08

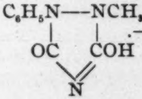
Barium Salt.—By titrating 0.5 gram phenylurazole with 29.5 cc. N/10 barium hydroxide, using phenolphthaleïn as indicator, and evaporating nearly to dryness and cooling, the barium salt crystallized out in plates, which were washed with alcohol and dried in the air. It decomposes at 280° to 300° without charring. There are 2 molecules of water of crystallization.

0.1970 gram substance heated five hours at 120° lost 0.0136 gram.

0.2065 gram salt required 7.82 cc. N/10 potassium sulphate and N/10 potassium bichromate to precipitate the barium and give a yellow solution.

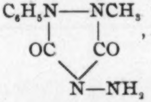
	Calculated for $(C_8H_6N_3O_2)_2Ba + 2H_2O$.	Found.
H_2O	6.86	6.90
Ba	26.16	26.01

1-Phenyl-2-methyl-3-hydroxyurazole,



.—This

substance was first made by Busch and Heinrichs[1] by the action of nitrous acid on 1-phenyl-2-methyl-4-aminourazole,



(see theoretical part). By heating phenylurazole in alcoholic potash with one molecule of methyl iodide three hours, with a return condenser, evaporating off the alcohol and acidifying, a precipitate of fine needles, which melt at 183°, is obtained. The substance is readily soluble in alkalies, ether and alcohol, and is somewhat soluble in cold water. By evaporating to dryness twice with concentrated hydrochloric acid, the body which melts at 183° is recovered unchanged, showing that the methyl group is attached to nitrogen and does not form the methoxy group, as Busch and Heinrichs supposed. This same methyl derivative, mixed with phenylurazole, is obtained by boiling the silver salt of phenylurazole with an alcoholic solution of methyl iodide with a return condenser for five hours. The substance is a monobasic acid giving a sharp reaction with 1 molecule of sodium hydroxide (phenolphthaleïn), and forming a mono-silver salt.

0.1382 gram substance required 7.26 cc. N/10 sodium hydroxide instead of 7.23 cc., calculated.

Analysis:

0.1096 gram substance gave 22.35 cc. nitrogen at 24° and 736 mm.

	Calculated for $C_9H_9N_3O_2$.	Found.
N	22.03	22.12

Silver Salt.—This is made by adding silver nitrate to the solution of the sodium salt and boiling. The precipitate is then readily filtered, and when dry melts at 250°, giving off strong fumes of an isocyanate. The salt is very soluble in ammonium hydrate, but insoluble in dilute nitric acid. When heated fifteen minutes with hydrochloric acid, filtered from the silver chloride, and evaporated, crystals of the 1-phenyl-2-methylurazole, which melts at 183°, are obtained.

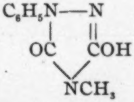
---

[1] Busch and Heinrichs: Ber. d. chem. Ges., 33, 455.

Analysis:

0.1566 gram silver salt gave 0.0570 gram silver.

	Calculated for $C_9H_8N_3O_2Ag$.	Found.
Ag	36.20	36.40

1-Phenyl-4-methylurazole,  .—This was made by a method which could not give the 1-phenyl-2-methylurazole. When molecular proportions of phenylsemicarbazide and methylacetylurea are melted together and heated two hours to 200°, ammonia and acetic acid are evolved and the mass becomes pasty. By dissolving in warm, dilute alcohol, cooling and filtering, 20 per cent of 1-phenyl-4-methylurazole is obtained. Its melting-point is 225°. The compound gives a violet color with alcoholic ferric chloride and gives mono-sodium and silver salts. By repeated evaporation with concentrated hydrochloric acid the melting-point is not changed. As the methyl group in this compound can only be at 4, it is evident that the methylation of phenylurazole by means of methyl iodide and alkalies takes place at 2, the hydrogen at this place seeming to be replaced more readily by methyl, acetyl, etc.

Analysis:

I. 0.1029 gram substance gave 21.5 cc. nitrogen at 28° C. and 730 mm.

II. 0.0420 gram substance gave 8.5 cc. nitrogen at 27° C. and 732 mm.

	Calculated for $C_9H_9N_3O_2$.	Found. I.	Found. II.
N	22.02	22.00	21.50

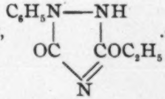
Silver Salt.—This was made by adding the requisite amount of silver nitrate to a solution of the neutral sodium salt, and boiling. Upon filtering and drying, there is obtained a stable silver salt, which melts at 225°, with decomposition, giving an isocyanate odor.

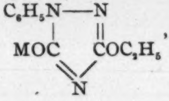
Analysis :

I. 0.1067 gram silver salt gave 0.0393 gram silver.

II. 0.0516 gram silver salt gave 0.0191 gram silver.

	Calculated for $C_9H_8N_3O_2Ag$.	Found. I.	Found. II.
Ag	36.24	36.83	37.01

1-Phenyl-2-hydro-3-ethoxyurazole, 

.—When the silver salt of phenylurazole, suspended in benzene, is treated with ethyl iodide in the cold for ten days, the reaction is complete. Upon filtering and evaporating off the benzene there is obtained an oil that gradually solidifies. Its melting point is about 141°. It is easily soluble in ether, benzene, alcohol, and slightly soluble in ligroin, but is insoluble in water and alkalies. Even boiling with concentrated caustic potash fails to effect solution. On the other hand, by evaporation with alcoholic hydrochloric acid, the ethoxy group is saponified and pure phenylurazole, melting at 264°, is obtained. Boiling this ethoxy compound with alcoholic potash and methyl iodide, with a return condenser, fails to methylate at the position 2. Upon evaporation, the oily ethoxy compound is recovered, which yields, when treated with hydrochloric acid, the phenylurazole that melts at 263°. An attempt was made to prepare this ethoxy compound by letting phenylurazole stand for one month in absolute ethyl alcohol containing 3 per cent of gaseous hydrochloric acid, but only unchanged phenylurazole was obtained. The question of the constitution of phenylurazole depends upon whether this ethoxy derivative is soluble in alkalies or not. A substance with the above formula cannot be soluble in alkalies, whereas the isomeric 1-phenyl-3-ethoxy-4-hydrourazole[1] is readily soluble in alkalies forming salts : 

, and is reprecipitated by acids.

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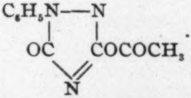
[1] Wheeler : J. Am. Chem. Soc., **22**, 377 (1900).

Analysis :

0.3616 gram substance gave 19.3 cc. nitrogen at 29° C. and 732 mm.

	Calculated for $C_{10}H_{11}N_3O_2$.	Found.
N	20.59	20.10

1-Phenyl-2-hydro-3-oxyacetylurazole,



This compound was made by allowing acetyl chloride to act upon the silver salt of phenylurazole in benzene solution in the cold. By filtering off the silver chloride, and evaporating off the benzene and acetyl chloride, an oil was obtained that would not solidify.

Analysis :

0.1301 gram substance gave 23.36 cc. nitrogen at 22° C. and 724 mm.

	Calculated for $C_{10}H_9N_3O_3$.	Found.
N	19.21	19.35

When it was dissolved in boiling dilute alcohol and heated for a few minutes, or if the water solution was allowed to evaporate in a desiccator, only the phenylurazole melting at 263° was obtained. Hot acids and alkalies saponify the body almost instantly. By its method of formation this compound must be the 1-phenyl-2-hydro-3-oxyacetylurazole, and the isomeric N-derivative,[1] which melts at 175°, must be the 1-phenyl-2-acetyl-3-hydroxyurazole, while the diacetylphenylurazole, melting at 164°, must be the 1-phenyl-2-acetyl-3-oxyacetylurazole. By boiling with water it loses, as we should expect, the O-acetyl at 3, giving the 2-N-acetylphenylurazole melting at 175°.

When 3-oxyacetyl-5-styryltriazol-1-propionic acid, which melts at 168°[2] is boiled two hours with a return condenser with 50 per cent alcohol, 3-hydroxy-5-styryltriazole-1-propionic acid, which melts at 243°, precipitates out on cooling.

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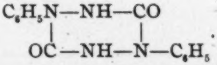
[1] Thiele and Schleussner : Ann. Chem. (Liebig), **295**, 171 ; Cuneo : Centrbl., 1898. I., 38.

[2] Bailey and Acree : Ber. d. chem. Ges., **33**, 1520.

When the ethyl 3-oxyacetyl-5-phenyltriazole-1-propionate, which melts at 80°, is treated in the same way, there is obtained the ethyl 3-hydroxy-5-phenyltriazole-1-propionate, which melts at 168°. Since these acetyl derivatives have been proved to be oxy compounds, this easy hydrolysis is to be expected.

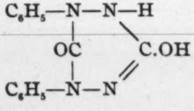
The comparison of the relative amount of hydrolysis of the isomeric N- and O-acyl derivatives of isatine, phenylurazole, phenyl mono- and dithiourazoles, and of urazole fatty acids will be taken up and studied quantitatively, and we wish to have this work left to us.

Diphenylurazine.—Work was started to determine the constitution of diphenylurazine. This compound was first made by Pinner[1] by heating phenylsemicarbazide, and then by Heller[2] by heating phenylcarbazinic ester. Pinner ascribed to this compound the symmetrical constitution :

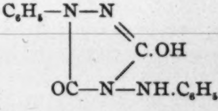


Such a compound should be a dibasic acid and give a disilver salt. But diphenylurazine is a monobasic acid, giving a violet color with alcoholic ferric chloride, combining with 1 molecule of caustic soda, and forming a monosilver salt, although giving a diacetyl derivative. Hence we seem to have a compound with an unsymmetrical constitution and it can be only

I.



or II.



.

Recent work by Rupe and Gebhardt[3] seems to confirm formula I, and we will not continue this work.

Pinner states that diphenylurazine, which melts at 264°, is changed by boiling alkalies into an isomeric form, which melts at 231°. This is a mistake. When boiled with an excess of caustic potash for one hour and acidified, only pure diphenylurazine, melting at 264°, was obtained.

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[1] Pinner: Ber. d. chem. Ges., **21**, 1225.

[2] Heller: Ann. Chem. (Liebig), **263**, 382.

[3] Rupe and Gebhardt: Ber. d. chem. Ges., **32**, 10.

Diphenylurazine does not titrate sharply against one molecule of sodium hydroxide (phenolphthaleïn).

0.3055 gram substance required 7.46 cc. N/7 caustic potash, instead of 7.97 cc., calculated.

0.1568 gram substance required 3.91 cc. N/7 caustic potash, instead of 4.09 cc., calculated.

Silver Salt.—When silver nitrate is added to a solution of the sodium salt of diphenylurazine and boiled, an amorphous precipitate of the monosilver salt is obtained. This is fairly stable toward light, and when heated darkens at 188° and decomposes at 204°, giving off isocyanate fumes.

Analysis :

0.2264 gram substance gave 0.0648 gram silver.

	Calculated for $C_{14}H_{11}N_4O_2Ag$.	Found.
Ag	28.77	28.62

UNIVERSITY OF UTAH,
December 1, 1901.

THE CONVERSION OF ORTHOPERIODIC ACID INTO NORMAL PERIODIC ACID.

BY ARTHUR B. LAMB.

While perchloric acid, its anhydride, monohydrate, and dihydrate are known, only the dihydrate of periodic acid has as yet been described. Bengiesser,[1] to be sure, states that the crystalline acid, H_5IO_6, loses its water of crystallization at 160° and does not decompose into oxygen and iodic anhydride until a temperature af 190° is reached. In other words, he states that periodic anhydride is formed at 160° and remains undecomposed at a temperature as high as 190°. Langlois[2] found that only at 200° is all the water eliminated, iodic anhydride and oxygen being formed at the same time.

Rammelsberg,[3] however, studied the effect of heat on the acid most carefully and arrived at quite different results. He

[1] Ann. Chem. Pharm., **17**, 254.

[2] J. prakt. Chem., **56**, 36.

[3] *Ibid.*, **103**, 281.

found that between 130°, the melting-point of the acid, and 136°, slow decomposition takes place, iodic anhydride, oxygen, and water being formed. From this he concludes that the preparation of periodic anhydride in this way is impossible.

It seemed probable, however, that if the acid were heated in a vacuum it might be possible to separate the point of dehydration from that of decomposition.

In the vacuum drying apparatus used, a constant temperature was maintained by the vapor of a boiling liquid. This temperature was, of course, variable at will by a change of liquids. The air entering the apparatus was dried by passing through tubes containing, first, calcium chloride and soda lime, then sulphuric acid, and finally, phosphoric anhydride.

The dihydrated acid, H_5IO_6, was prepared as follows: Chlorine was passed into a concentrated solution of sodium iodate and hydrate. Trihydrogen sodium periodate,

$$Na_2H_3IO_6,$$

was thereby precipitated (Magnus and Ammermüller).[1]

Silver nitrate converted an acid solution of this salt into the silver salt, from which the free acid was secured by treatment with bromine (Kämmerer).[2] The resulting aqueous solution of the acid, after having been evaporated as completely as possible on the water-bath, was dried to constant weight by standing several days over strong sulphuric acid and phosphoric anhydride. To establish the purity of this acid it was analyzed. The original distillation method of Bunsen[3] was used, not, however, until fruitless attempts had been made to secure concordant results by the method of analysis used by Kimmins.[4]

I. 0.0464 gram liberated 0.15888 gram iodine.
II. 0.0493 gram liberated 0.16350 gram iodine.

	Calculated for H_5IO_6.	Found.	
		I.	II.
I	55.60	55.32	55.29

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[1] Pogg. Ann., **28**, 514.

[2] J. prakt. Chem., **79**, 94.

[3] Ann. Chem. (Liebig), **86**, 265.

[4] J. Chem. Soc. (London), **51**, 361; **55**, 154.

A portion of the acid had been tested with silver nitrate and nitric acid, but only a trace of iodic iodine had been found.

Taking samples of this acid, using water in the vapor jacket of the drying apparatus, and a pressure of 12 mm., a constant weight was in general secured after heating from twenty to twenty-five hours. The drying process was interrupted when the loss, after several hours, amounted to but a fraction of a milligram. This was necessary since sublimation became apparent upon the walls of the drying chamber after ten or twelve hours of heating, and experiment showed that such slight losses would continue indefinitely.

No.	Substance heated. Gram.	Loss in weight. Gram.	Loss in weight. Per cent.
I.	0.4055	0.0642	15.83
II.	0.4842	0.0747	15.43
III.	0.8673	0.1357	15.59
		Mean,	15.62

	Per cent.
Calculated loss for H_3IO_5	7.91
" " " HIO_4	15.74
" " " I_2O_7	19.79

These numbers point with certainty to the composition HIO_4.

Qualitative tests of this dehydrated acid showed the presence of slightly more iodic iodine than was present in the original acid. To confirm the above conclusions, based on the loss of weight, analyses from samples of the above dehydration, experiment III., were made :

No.	Acid. Gram.	Iodine liberated. Gram.	Iodine liberated. Per cent.
I.	0.0966	0.37761	65.16
II.	0.0500	0.19651	65.50
III.	0.c677	0.26407	65.22
		Mean,	65.29

	Per cent.
Calculated per cent of iodine in H_3IO_5	60.45
" " " " " " HIO_4	66.12
" " " " " " I_2O_7	69.37

Analysis therefore confirms the conclusion that the acid formed by the dehydration method under the above conditions was the compound represented by HIO_4.

This normal periodic acid was white or slightly yellowish in color. When dropped into water, sufficient heat was generated to occasion audible hissing.

Higher temperatures were now tried, in the hope of securing periodic anhydride. Toluene, boiling at 110°, was substituted for water in the drying apparatus. Sublimation became more apparent on the walls of the drying chamber, but no loss in weight occurred beyond that evidently due to this cause. Tests indicated the presence of somewhat more iodic iodine than was present in the acid dried at 100°.

Substituting xylene, boiling at 138°, marked sublimation occurred, accompanied by a rapid loss in weight. Large amounts of iodic anhydride were now found to be present. This agrees with the statement of Rammelsberg quoted above.

To determine whether a vacuum had any detrimental effect at these high temperatures, a sample of the normal acid was treated at atmospheric pressure in the drying apparatus, using toluene in the vapor jacket. The acid lost rapidly in weight, and much iodic anhydride was formed. After thirty hours' heating the loss in weight indicated that if partial decomposition had taken place into iodic anhydride, oxygen, and water, approximately 40 per cent of the resultant mixture should be iodic anhydride. Analyses were made by Bunsen's method, and the relative amounts of iodic anhydride and normal periodic acid were calculated on the assumption that nothing else was present.

I. 0.1332 gram liberated 0.48918 gram iodine = 31.1 per cent of I_2O_5.

II. 0.1094 gram liberated 0.40033 gram iodine = 33.3 per cent of I_2O_5.

The percentage amounts of iodine in iodic anhydride and in normal periodic acid are so nearly the same (76.1 per cent and 66.1 per cent, respectively) that the slightest difference in the amount of iodine liberated was magnified many times in the calculation.

In addition to heat, several other means were employed to dehydrate normal periodic acid, but without success. Acetyl chloride added to the acid reacted violently even at —20° ; if the acid was added to the chloride the reaction was less energetic. A clear, cherry-red solution was obtained in either case, which, added to water, showed complete reduction to the iodic condition. If acetyl chloride were added to a solution of the normal acid in glacial acetic acid, a white flocculent precipitate appeared. This also, when filtered off and washed, showed complete reduction to the iodic condition. When dried in a vacuum at 100° and analyzed, the following numbers were obtained.

0.0844 gram liberated 0.25191 gram iodine.

	Calculated for I_2O_5.	Found.
I	76.1	74.6

Acetic anhydride also reacts with the acid vigorously at ordinary temperatures, but slowly in the cold. Evolution of a gas takes place and the reaction-product showed, on the addition of water, complete reduction to the iodic condition.

Anhydrous perchloric acid also decomposed the acid, even at low temperatures.

Repeated attempts were also made to secure the intermediate hydrate, H_3IO_5, by drying.

1. At a temperature of 67° and a pressure of 17 to 18 mm.
2. At a temperature of 55° to 64° and a pressure of 27 mm.[1]
3. At a temperature of 44° to 49° and a pressure of 24 mm.

In all three experiments the point corresponding to the hydrate, H_3IO_5, was passed without the least indication of the formation of a definite compound, though in the two latter experiments the rate of dehydration was exceedingly gradual; in the second, fifty hours, in the third, one hundred hours being required to pass the point in question. It appears impossible to secure this intermediate hydrate by simple drying.

The author wishes to thank Prof. A. Michael for his suggestion of the research and valuable assistance in its execution.

TUFTS COLLEGE, MASS.

[1] In the second and third experiments a water-bath was used as jacket for the dehydration vessel, which latter contained, besides the substance, a thermometer and a manometer.

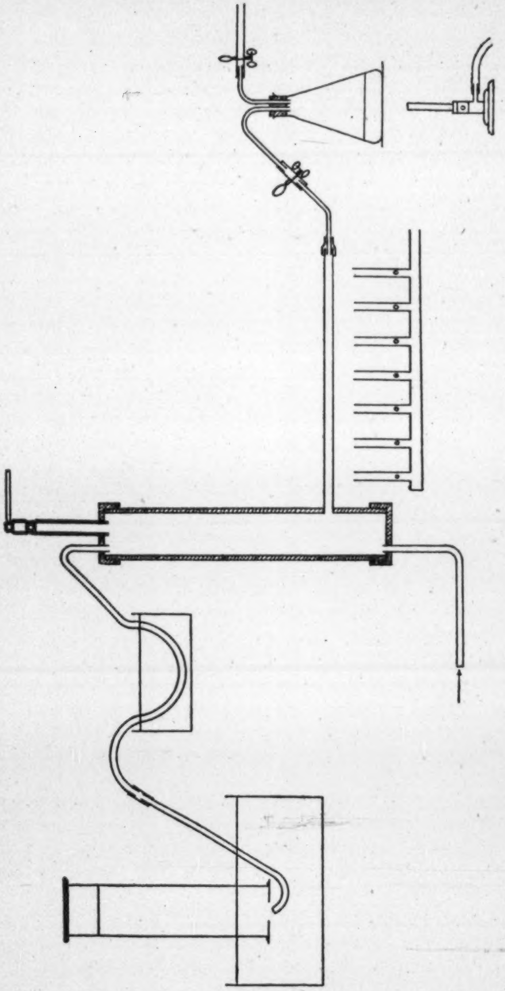
A SIMPLE APPARATUS FOR DEMONSTRATING THE MANUFACTURE OF WATER-GAS.

BY C. E. WATERS.

The great advantage of being able to demonstrate the manufacture of water-gas as a lecture experiment is so obvious that a form of apparatus was devised which works very successfully. A piece of heavy, two-inch iron pipe is provided with caps, screwed on the ends. Into the lower one is screwed a piece of pipe, of one-fourth inch bore, bent at a right angle, and connected by a rubber tube with an oxygen-cylinder. About 3 inches above the base, is screwed in a quarter-inch pipe about 2 feet 6 inches or three feet long. To this is attached an Erlenmeyer flask, which serves as the steam generator. By a simple arrangement of spring pinch-cocks the steam can be passed through the pipe or allowed to escape into the air. Into the upper cap is screwed a short piece of half-inch pipe, which has a quarter-inch hole bored through close to the upper end. This hole may be closed by screwing down a cap which is provided with a suitable handle. A large pair of gas-pliers could be used instead of the handle. Into a second hole in the upper cap is screwed the delivery tube of quarter-inch pipe, which carries the gas into a pneumatic trough, where it may be collected in cylinders. It is advisable to use a glass tube at the outer end of the delivery tube, and to avoid burning the rubber connection it is well to have the pipe bent into a U, which dips under cold water contained in a crystallizing-dish.

The large pipe is sheathed inside and out with several layers of asbestos paper, and the caps are provided inside with perforated disks of asbestos board to protect the iron as much as possible. The bottom of the pipe is also filled with fragments of tile to a depth of 2 inches.

The experiment is carried out in the following manner: A fuse made of loosely-twisted cotton string is pushed in through the side opening. Then small fragments of charcoal, fine



coke, and finally ½ to ¾-inch pieces of coke are poured in at the top until the large pipe is nearly filled. The upper cap is replaced and the whole is then supported on a stand, using one small ring at the bottom and a larger one at the middle. It is well to use a clamp at one of the upper pipes also. It is placed close to the end of a combustion furnace, and at such a height that the horizontal tube will lie in the trough when screwed into place. The Erlenmeyer flask is placed in position and the water heated to boiling by a small flame. The furnace should also be lighted. When all is ready the fuse is lighted, a slow current of oxygen is passed in through the tube at the bottom, the lateral tube is screwed in place, and all connections are made. For the "hot blast" the hole in the side of the upper tube should be open. An increased current of oxygen is passed in until the outer layer of asbestos becomes very hot. Then the oxygen is shut off, the upper opening closed, and by adjusting the pinch-cocks steam is passed through the horizontal pipe, which should be heated nearly to redness. As soon as this superheated steam reaches the hot coke there is quite a rapid evolution of gas, which is collected in cylinders. In a few moments no more comes over, and the steam is to be shut off from the furnace and the outer pinch-cock is opened; the upper outlet is reopened, and oxygen is run in as before. The operation can, of course, be repeated until the coke is consumed.

The gas is at first clouded, but soon becomes clear. It burns with a pale-blue flame. It is a simple matter to enrich it by causing it to bubble through benzene, or some similar hydrocarbon, contained in a wash-bottle. Working on such a small scale, it is not to be expected that the gas would have the same composition as that made commercially. Analysis showed that it is true water-gas, and not simply carbon monoxide forced over by the entering steam. To make sure that the hydrogen was not formed in the superheating tube, we raised the temperature of this tube still further and passed the steam into water. The gas which was collected gave no evidence of containing hydrogen.

Analysis of Water-Gas.

	I.	II.	III.	IV.
CO_2	19.2	40.3	31.7	33.8
O_2	0.8	0.2	1.5	0.0
CO	43.8	19.0	27.4	31.1
H_2	27.1	29.1	31.3	29.1
N_2	9.1	11.4	8.1	6.0

These figures become more nearly comparable when recalculated on the basis of a mixture from which the carbon dioxide has been removed.

	I.	II.	III.	IV.
O_2	0.9	0.3	2.3	0.0
CO	52.6	32.3	41.1	46.7
H_2	32.5	49.5	47.0	43.7
N_2	10.9	19.4	12.2	9.0

The oxygen which was used was found to contain about 8 per cent of nitrogen. The varying proportions of carbon monoxide and hydrogen may be due to the considerably greater solubility of the former in water, which would make quite a difference when only small quantities of the water-gas are made.

JOHNS HOPKINS UNIVERSITY,
December, 1901.

Contribution from the Chemical Laboratory of Purdue University.

DICHLORACETYL PHOSPHIDE.

BY P. N. EVANS AND C. E. VANDERKLEED.

In a general survey of the classes of organic compounds one is struck by the fact that in spite of the recognized analogy in properties between the amines and phosphines, reference to the phosphorus derivatives corresponding to the acid amides is entirely lacking in most text-books, presumably on account of the very small number of representatives of this class known. Apparently only two of these bodies, which may appropriately be called *phosphides*, have been prepared and examined, namely, monochloracetyl phosphide[1] and trichloracetyl phosphide.[2]

The purpose of the work here presented was to add to our knowledge of this class of compounds.

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[1] Steiner: Ber. d. chem. Ges., **8**, 1178 (1875).

[2] Cloëz: Ann. chim. phys., [3], **17**, 309.

Since the readiness of formation and the stability of these substances depend on the acid character of the organic radical and the basic properties of the PH_2 group, it can be foreseen that the phosphides will be less readily prepared and less stable than the corresponding amides, on account of the more weakly basic character of phosphorus than of nitrogen in the hydrogen compounds, and those phosphides will be most easily made whose organic radicals are most strongly acid.

Of the many methods used to prepare amides, the reaction involving the treatment of an acid chloride with ammonia takes place most vigorously and generally, and therefore the analogous method seemed most promising for the preparation of the phosphides; and this was the reaction employed in the cases already successfully investigated, previously mentioned. Some preliminary experiments with phosphine (PH_3) and chlorides of some of the commoner acids by one of the authors have given unpromising results, solid phosphorus hydride being produced, but it is hoped to further examine these cases soon. It seemed desirable, therefore, for the sake of experience, to select an acid that might reasonably be expected to give positive results, and since mono- and trichloracetic acids had already given the desired products in other hands, the intermediate dichloracetic acid was selected. Acetic acid itself had presented difficulties under experiment, but the greatly increased acid character due to chlorination gave hope of better results with the chloracetic acids.

Preparation of Materials.

The materials required were dichloracetyl chloride, $CHCl_2COCl$, and gaseous hydrogen phosphide, PH_3.

Dichloracetyl Chloride.—This involved the preparation of potassium dichloracetate from potassium ferrocyanide and chloral hydrate by heating in water,[1] the liberation of dichloracetic acid from the potassium salt by means of hydrochloric acid gas,[2] and the conversion of the acid into the acid chloride by treatment with phosphorus trichloride.[3]

The details of the preparation were as follows:

[1] O. Wallach: Ber. d. chem. Ges., **10**, 1526 (1877).

[2] O. Wallach: *Ibid.*, **9**, 1213 (1876).

[3] R. Otto and H. Beckurts: *Ibid.*, **14**, 1618 (1881).

Potassium Dichloracetate.—One hundred and seventy grams potassium ferrocyanide and 115 grams chloral hydrate were dissolved in 500 cc. water in a flask with reflux condenser, and heated until the color of the ferrocyanide disappeared (about two hours), a green precipitate of a double cyanide of iron and potassium, $KFe(CN)_3$, separating and being filtered off from time to time to prevent bumping. When the reaction was complete the mixture was cooled and filtered, and then heated to prove that no further precipitation occurred. The filtrate was then evaporated to dryness on the water-bath and the potassium dichloracetate extracted from the potassium chloride with about 450 cc. strong alcohol in several portions; the alcoholic extract was evaporated to dryness on the water-bath and the residue dried at 105°. The reaction is represented by the equation

$$2K_4Fe(CN)_6 + 3CCl_3CHO.H_2O = \\ 3CHCl_2COOK + 3KCl + 2KFe(CN)_3 + 6HCN,$$

and the yield was about 70 per cent of the theoretical.

Dichloracetic Acid.—The dried potassium dichloracetate was placed in a piece of ordinary combustion tubing held nearly horizontal and connected by a long adapter at its lower end with a dry flask; a current of dry hydrochloric acid gas was passed through from the upper end and the tube gently heated till the gas escaped from the flask; then the temperature was raised till all the dichloracetic acid, boiling at 190°, had distilled into the flask. The yield was about 70 per cent of the theoretical.

Dichloracetyl Chloride.—Fifty grams of dichloracetic acid and 30 cc. phosphorus trichloride were warmed together with reflux condenser as long as hydrochloric acid was evolved, and then the dichloracetyl chloride, boiling at 107°, distilled off. The yield was about 60 per cent of the theoretical.

Gaseous Hydrogen Phosphide.—Two hundred and fifty grams potassium hydroxide were dissolved in 500 cc. strong alcohol and placed in a liter flask, and 50 grams yellow phosphorus added; after displacing the air in the flask with illuminating gas, a gentle heat was applied and the gas, about 20 liters, conducted into a gas-holder for use. Prepared in this way it is not spontaneously inflammable and contains about equal volumes of the phosphide and hydrogen.

Preparation of Dichloracetyl Phosphide.

The hydrogen phosphide, after being dried by passing through a tube about a meter long filled with soda-lime, was passed slowly through the dichloracetyl chloride contained in a small flask for several hours, the liquid becoming somewhat yellow and more and more viscous until the gas no longer passed through in bubbles but formed a channel. When this condition was reached, several times the volume of anhydrous ether, free from alcohol, was added. On standing some hours, with occasional shaking, the gummy mass was changed to a yellowish-white powder, which was filtered off, washed with ether, dissolved in a very small quantity of alcohol, again filtered and reprecipitated with ten or more volumes of ether, being allowed to stand several hours. The faintly yellow powder was filtered off, washed with ether, dried in a vacuum desiccator, and finally at 100°.

Attempts to prepare the phosphide by passing the gas into a solution of the acid chloride in ether and in benzene gave the product as a suspended powder, but the yield was poorer than when the solvents were not employed.

Analysis of the Product.

A qualitative examination showed charring on heating, with evolution of a substance with a phosphorus-like odor, and on ignition with copper oxide a bluish-green flame coloration, indicating the presence of carbon, phosphorus, and chlorine.

Quantitative estimations of phosphorus and chlorine were made to confirm the supposed formula, $CHCl_2COPH_2$, which corresponds to phosphorus 21.37 and chlorine 48.96 per cent.

Phosphorus was estimated by the Carius method and satisfactory figures obtained; but the same method for the simultaneous estimation of chlorine gave variable results, in all cases lower than the proportion required by the formula, so the method of igniting in an open tube with lime was employed, with satisfactory results.

In the phosphorus estimation, the material (about 0.2 gram) was heated in a sealed tube with fuming nitric acid and silver nitrate (for the chlorine) to 200° for eight hours, the silver chloride filtered out, the remaining silver precipitated with hydrochloric acid and removed, then the phosphoric acid precipitated with ammonium molybdate, and finally with magnesia mixture and weighed as pyrophosphate.

0.1530 gram substance gave 0.1218 gram $Mg_2P_2O_7$, corresponding to 22.2 per cent phosphorus. A second analysis gave practically the same result.

In the chlorine estimation the substance (about 0.05 gram) was mixed with lime and heated in a combustion tube for an hour or more, then the mixture dissolved in dilute nitric acid, filtered, and the chlorine precipitated as silver chloride with silver nitrate.

0.0493 gram substance gave 0.0932 gram AgCl, corresponding to 46.55 per cent chlorine; and 0.0479 gram substance gave 0.0930 gram AgCl, corresponding to 48.01 per cent chlorine.

These figures, while not as exact as desired, leave hardly a doubt as to the identity of the product examined.

Properties of the Phosphide.

Dichloracetyl phosphide is a faintly yellowish-white crystalline powder with a slight odor resembling the free acid and hydrogen phosphide, apparently due to slow decomposition due to moisture. Heated to 200° C., it chars without melting. It is nearly or quite insoluble in ether, benzene, chloroform, and petroleum ether; insoluble in cold water, but soon decomposed by it with evolution of hydrogen phosphide; very soluble in strong alcohol, the solution acquiring, after a time, a fruit-like odor, probably due to a decomposition resulting in the formation of the ethyl ester of the acid; in absolute alcohol it is very soluble without apparent decomposition.

The preparation of other acid phosphides by similar reactions is being carried out successfully and will be reported in a later paper.

LAFAYETTE, INDIANA,
December, 1901.

REPORTS.

On the Present State of the Chemistry of Albumin.[1]

The chemical investigation of the vegetable and animal organs has shown that certain elements and atomic groups are present in all living parts. We must assume that the phenomena of life are possible only in their presence, that they are based upon chemical and physical changes of these constituents. The albumins are so prominent among these substances that some investigators have regarded them as the true basis of vital phenomena. Their great physiological importance has led chemists and physiologists to study their properties and reactions and to attempt to learn their chemical structure. Given a knowledge of their chemical structure, it would be possible to form an opinion in regard to the part played by them in the life processes.

In investigating albumins they have been subjected to hydrolysis and to oxidation. The first products of the breaking-down process are larger atomic groups—*albumoses*, *propeptones*, *peptones*. Further decomposition gives smaller atomic groups which are very stable towards some hydrolyzing agents. These latter products may be regarded as the building-stones of the albumin molecule.

There are certain albumins which, by gentle action of the decomposing agent used, break down into two parts, of which one is again an albumin, while the other is an organic or inorganic, but not albuminoid, atomic group. We must assume that in these cases the latter group is imposed upon an albumin molecule. The group thus split off from the albumin has been called a *prosthetic group*. The complex albumins that break down in this way into an albumin and a prosthetic group have been called *proteids* by Hoppe-Seyler. There is no doubt that many, if not most, of the atomic complexes that are active in the organisms are unstable compounds of albumin with other organic bodies.

When stronger chemical agents are allowed to act upon the albumin that is split off from the prosthetic group, another group of cleavage products is obtained. Lossen[2] oxidized egg albumin with potassium permanganate in the presence of magnesium sulphate and obtained guanidine. In 1890 Drechsel[3] studied the action of boiling baryta water on *lysatine*, a crystalline product formed by the action of aqueous hydrochloric acid on albumins, and obtained urea. This led him to believe that lysatine is the substance from which guanidine is formed in the oxidation of albumin. But Hedin showed that lysatine consists of *arginine* and *lysine*. E. Schulze and his pupils have shown that arginine, which occurs in nature in certain sprouts, yields urea and a compound of the formula $C_5H_{12}N_2O_2$ when treated with baryta water. When the compound $C_5H_{12}N_2O_2$ is treated with cyanamide, arginine is regenerated. The compound $C_5H_{12}N_2O_2$ turned out to be *ornithine*, a substance that had long been known as a product of animal metabolism. Ornithine has been shown to be 1,4-diamidovaleric acid. Quite recently E. Fischer[1] has succeeded in preparing a 1,4-diamidovaleric acid that is evidently the inactive form of ornithine. The relations between creatine, arginine, ornithine, and putrescine are represented by the following formulas :

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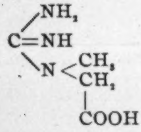
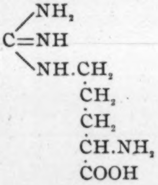
[1] Abstract of a lecture by A. Kossel, delivered before the German Chemical Society, June 1, 1901. See Ber. d. chem. Ges., **34**, 3214.

[2] Ann. Chem. (Liebig), **201**, 369 (1880).

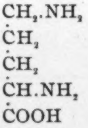
[3] Archiv. f. Anatomie u. Physiologie, Physiol. Abth., 1891, p. 248.



Creatine.

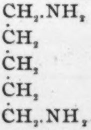


Arginine.



$$\begin{array}{l} CH_2.NH_2 \\ \dot{C}H_2 \\ \dot{C}H_2 \\ \dot{C}H.NH_2 \\ \dot{C}OOH \end{array}$$

Ornithine.



$$\begin{array}{l} CH_2.NH_2 \\ \dot{C}H_2 \\ \dot{C}H_2 \\ \dot{C}H_2 \\ \dot{C}H_2.NH_2 \end{array}$$

Putrescine.

Lysine has been shown by Drechsel to be α,ε-diamidocaproic acid, and the same chemist has found diamidoacetic acid among the decomposition products of albumin. Finally, *histidine*, a substance of the formula $C_6H_9N_3O_2$, belongs to this same group of basic cleavage products of albumin.

The next group of cleavage products of albumin is that of the monamido acids. The simplest compound of this group is glycocoll, which is very frequently met with. The next member of the group of amido acids, *alanine*, or α-amidopropionic acid, has been found among the decomposition products of fibroïn from silk. But the derivatives of this acid, formed by oxidation, or by the introduction of sulphur, or by the addition of an aromatic group, are of greater importance than the acid itself. Among these are *serine* obtained from silk, and *cysteïne* obtained from *cystine*. The relations between these substances have been clearly established. They are represented by the following formulas :

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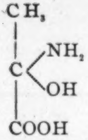
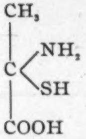
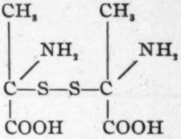
[1] Ber. d. chem. Ges., 34, 454 (1901).



Serine.



Cysteïne.

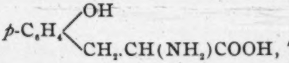


Cystine.

Recently, Mörner[1] has shown that when horn is treated with hydrochloric acid two cystines are formed, a laevorotatory and a dextrorotatory variety.

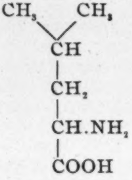
Other derivatives of amidopropionic acid that are obtained from albumin contain an aromatic nucleus. *Phenylalanine* (phenyl-α-amidopropionic acid) which was first found in sprouting plants, and later as a product of the cleavage of vegetable albumins, is one of these. Another is ***tyrosine***, which was discovered by Liebig in 1848, and has since then been regarded as a characteristic cleavage product of albumins. Tyrosine is a laevorotatory *p*-hydroxyphenyl-α-amidopropionic acid. The relation between phenylalanine and tyrosine is shown by the formulas:

$C_6H_5CH_2.CH(NH_2)COOH$, Phenylalanine;

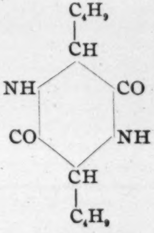


$$p\text{-}C_6H_4\begin{cases} OH \\ CH_2.CH(NH_2)COOH \end{cases}$$, Tyrosine.

An amidobutyric acid and an amidovaleric acid have been found among the cleavage products of albumin, but *leucine*, which is the laevo rotatory α-amidoisobutylacetic acid, is much more commonly and abundantly met with, and together with this a compound, $C_{12}H_{22}N_2O_2$, called *leucineimide*. This is to be regarded as a derivative of diacipiperazine formed by the combination of two molecules of leucine:



Leucine.



Leucineimide.

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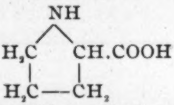
[1] Ztschr. physiol. Chem., **28**, 595.

Emil Fischer has recently found active pyrrolidine-α-carbonic acid among the decomposition products of caseïn:



Pyrrolidine-α-carbonic acid.

To the above-named amido acids and their derivatives, must be added aspartic acid, $COOH.CH_2.CH(NH_2).COOH$, and glutamic acid, $COOH.CH_2.CH_2.CH(NH_2).COOH$, as among the cleavage products of albumin.

Carbohydrates have repeatedly been obtained as prosthetic groups. That carbohydrate residues occur in the molecules of albumin appears probable from evidence furnished by investigations of Udransky.[1] This chemist has shown that when pure albumins are distilled with sulphuric acid furfurol is obtained. The formation of furfurol was regarded by him as evidence of the presence of a carbohydrate group in albumins. The cause of the formation of the furfurol has, however, not yet been determined.

When other chemical agents besides dilute acids or alkalies, such as enzymes, oxidizers, fusing alkalies, are used for the purpose of breaking down the albumin molecule, products are obtained that are essentially the same as those already mentioned, or they are such as can be formed by further transformation of these. Thus, the fatty acids that are formed when albumins are treated with fusing potassium hydroxide have their origin in the amido acids; paraoxybenzoic acid comes from tyrosine; and benzoic acid from that constituent of albumin that yields phenylalanine.

It is evident that all the atomic groups contained in the albumin molecule cannot be detected by hydrolysis by means of acids and alkalies. More energetic hydrolysis destroys that group which gives the biuret reaction—a red coloration caused by copper sulphate in the presence of caustic soda. The first decomposition products, which are similar to the original albumins, give this reaction very strongly. By further action of the hydrolyzing agent the reaction disappears, and we can therefore distinguish between products that give the biuret reaction and products that do not give the biuret reaction.

Just as the biuret-forming group disappears, so also one aromatic group of the albumin molecule disappears under the influence of dilute acids. When bromine acts upon albumins in the presence of water, tribromamidobenzoic acid is formed. Neither of the two aromatic groups which are obtained by simple hydrolysis contains an amido group in the benzene ring, and we must therefore assume, either (1) that, besides the tyrosine and the phenylalanine, a third aromatic group exists, or (2) that an atomic rearrangement takes place in these reactions. The first explanation is in harmony with the formation of indol and skatol. When fusing alkali acts upon albumins, or they are subjected to the action of microorganisms, indolcarbonic acid and skatolcarbonic acid are formed. Under some circumstances skatolacetic acid, besides paraoxyphenylacetic and phenylacetic acids, can be obtained in the decomposition of albumin :

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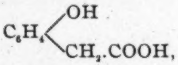
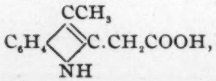
[1] Ztschr. physiol. Chem., **12**, 389.



$C_6H_4 < \begin{matrix} OH \\ CH_2.COOH \end{matrix}$, Paraoxyphenylacetic acid ;

$C_6H_5CH_2.COOH$, Phenylacetic acid ;



$C_6H_4 \langle \begin{matrix} CCH_3 \\ \\ NH \end{matrix} \rangle C.CH_2COOH$, Skatolacetic acid.

Nencki regards these three compounds as representatives of the three forms in which the benzene group is contained in the molecule of albumin.

The decomposition-products of albumin, according to the above, may be brought under four heads :

1. The urea-forming group to which arginine belongs.
2. The group of the diamido acids. Diamidovaleric acid is combined with the urea-forming group in arginine.
3. The group of the monoamido acids.
4. Finally, other products are obtained, the relations of which to the above groups are not yet known.

On the other hand, the number of albumins is very large. These can be distinguished between by differences in solubility, in their conduct towards precipitating reagents, and by other peculiarities. Every typical albumin of animal or vegetable origin gives most of the above-named groups. The molecule of albumin must therefore be of extraordinary complexity. The investigation of the structure of albumin would be extremely difficult even if the individuality and purity of the albumins were beyond all doubt. But this is far from being the case. And further, the albumins combine with other substances with the greatest ease. Of special importance is the fact that they combine with one another. This makes it appear probable that most of the albumins that have been isolated from animal tissues are complex compounds of several simpler albumins. A number of facts go to show that when the large molecule of albumin is broken down by hydrolysis, oxidation, or the action of enzymes, it yields (1) several smaller molecules (*albumoses*) which then break down into (2) still smaller biuret-forming atomic complexes (*peptones* in the modern sense), and finally into (3) the above-named products that do not give the biuret reaction.

Owing to the great difficulties encountered in the investigation of typical complex albumins, the author has tried to get light on the problem by seeking in nature for simpler albumins. Such substances are the protamines that are found in the spermatozoa of fish. The first member of this class was discovered thirty years ago by Miescher in the spermatozoa of the salmon. He described it as a substance of the formula $C_9H_{21}N_5O_3$, Kossel[1] later found basic compounds in the spermatozoa of other fishes. These resemble the protamine of the salmon or *salmine*, but are not identical with it. Such are *sturine* from the testicles of the sturgeon,[2] and *clupeine* from the testicles of the herring.[3]

The protamines are compounds of strong basic properties. They have a high molecular weight—at least the free bases do not raise the boiling-point of water. Hydrolysis has shown that there are several groups of these protamines. The simplest, salmine and clupeine, break down into arginine, amidovaleric acid, and a residue, the nature of which is not yet known. The quantity of arginine obtained from salmine is 84.3 per cent, from clupeine it is 82.9 per cent of the protamine taken. According to this, 87.8 per cent of the total nitrogen in salmine, and 83.5 per cent of that in clupeine, is in the form of arginine.

Each of the three protamines above named therefore contains three of the characteristic groups of the albumins—the urea-forming complex, diamidovaleric acid, and amidovaleric acid. That these groups are arranged in the protamines in a way similar to that in which they are arranged in the complex albumins appears probable from the fact that the protamines show the biuret reaction. The propeptones and peptones, as has been pointed out, are intermediate products that are formed when the original albumins are broken down into the abiuretic substances (substances that do not give the biuret reaction). Similar intermediate products are formed from protamines. These are called *protones*. The protamines, like the typical albumins, have colloidal properties, and they can easily be salted out. As they pass over into the protones these properties are gradually lost, as is the case in the peptonization of the albumins.

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[1] Verhandl. d. naturforsch. Gesell. in Basel, VI., Heft 1, ss. 138–208; Picard: Ber. d. chem. Ges., **7**, 1714 (1874).

[2] Ztschr. physiol. Chem., **22**, 176.

[3] *Ibid.*, **25**, 165.

In all attempts to bring the group of albumins into a chemical system the fact must be kept in mind that the molecule of albumin is composed of several like or unlike parts, the albumoses or peptones, a knowledge of which must be the first object of the investigation. In order to get a general conception of the constitution of the albumin molecule, it will be desirable to fix our attention upon some one group contained in the albumins, and to regard the albumoses and peptones as formed by the addition of different groups to this *nucleus*. We must, of course, for this purpose, select as this nucleus a group that is contained in all albumins or in as many as possible—even in the protamines. Arginine answers these conditions best. In this light, the simplest biuret-forming complexes, the protones and the protamines, are to be regarded as formed by the addition of a monamido acid, amidovaleric acid, and of another substance still unknown to the arginine group. In the case of the higher protamines there is, of course, greater complexity of the molecule.

The differences in the relative quantities of the various groups that go to make up the albumin molecule would suffice to explain the existence of a large number of albumins. Possibly other differences may be due to the arrangement of the constituent groups in space. At all events, it is clear that the conception of "albumin" as a factor of constant value, as always signifying the same thing, is unjustifiable.

It has been pointed out that, in the tissues and secretions of animals and plants, the albumins frequently occur in combination with other groups. The physical properties of these *proteids* are essentially those of the albumins, and hydrolysis is generally necessary to determine whether these substances consist of two constituents, an albumin, or at least a biuret-forming compound (peptone), and the prosthetic group.

The union of the albuminous constituent and the prosthetic group may be more or less firm. Hoppe-Seyler,[1] for example, has shown that in the yolk of eggs lecithine is combined with albumin very loosely, the compound being broken down even by hot alcohol. In other cases energetic action is required to effect this separation of the prosthetic group from the albumin.

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[1] "Physiologische Chemie," Berlin, 1877–81, p. 781.

In a few cases it has been possible not only to decompose the proteid into its constituents, but also to cause these constituents to combine to form the proteid. Altman,[1] for example, has shown that the prosthetic group of many nucleins, *nucleic acid*, gives with albumin a precipitate that has the properties of the original proteid, nuclein.

The prosthetic groups are of many kinds. An inorganic group, a phosphoric acid, for example, may combine with the biuret-forming complex ; in other cases a complicated organic group may be united with the albumin.

The glycoproteids have of late attracted the attention of physiological chemists. These are made up of a carbohydrate group combined with albumin, and investigations are now in progress involving these substances.

In the so-called nucleins the carbohydrate complex appears to be united with a large number of other atomic groups. In the nucleic acids at present known, different carbohydrates are undoubtedly contained. The other groups thus far found in the nucleic acids belong essentially to the pyrimidine group. The investigations of the last twenty years have shown that the derivatives of pyrimidines play a very important part in the fundamental vital phenomena. Kossel has found them in the place where the synthetical processes—the phenomena of growth—take place, that is to say, in the cell nucleus.

I. R.

The Dissociating Power of Liquid Hydrocyanic Acid.

A paper has just appeared by Centnerzwer[2] describing an investigation on the dissociating power of liquid hydrocyanic acid. This investigation was carried out under the guidance of Prof. Walden, whose work on non-aqueous solvents is so well known. After showing that liquid cyanogen has practically no dissociating power, it seemed desirable to study, in this connection, liquid hydrocyanic acid, and especially for the following reasons:

First: The nitriles CH_3CN, C_2H_5CN, etc., have strong dissociating power.

Second: In homologous series such as HOH, CH_3OH, C_2H_5OH, or HNH_2, CH_3NH_2, $C_2H_5NH_2$, the first member has much the strongest dissociating power.

Third: Hydrocyanic acid being the first member of the homologous series of nitriles should have especially strong dissociating power.

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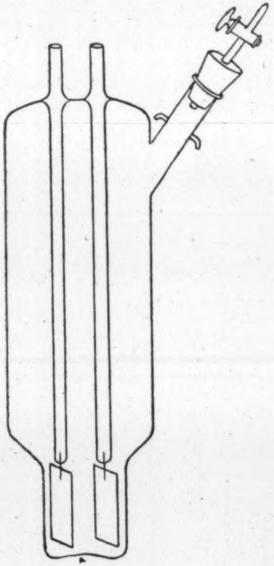
[1] Archiv. für. Anat. u. Physiolgie (physiol. Abtheilung), 1889, p. 524.

[2] Ztschr. phys. Chem., **39**, 217.

Fourth : Liquid hydrocyanic acid has been shown to have a very high dielectric constant, 95, while that of water, at the same temperature, is only about 80. From the relation pointed out by J. J. Thomson, and later by Nernst, between the dissociating power of a solvent and its dielectric constant, hydrocyanic acid should have a very high dissociating power.

The method employed in measuring the conductivity of the solutions is very simple. The apparatus is shown in the accompanying sketch :



A fairly concentrated solution of the salt in the solvent was prepared by bringing the two together in weighed quantities. This solution was introduced into the vessel and its conductivity determined. A part of the solution was then poured out through the stop-cock, and replaced by the pure solvent. The conductivity of the new solution was then determined and this process repeated until the most dilute solution was reached.

The conductivity of the solvent was found to vary somewhat, the purest specimen having the value 0.496×10^{-5} in reciprocal Siemens' units.

The conductivities of potassium iodide and trimethyl sulphonium iodide, in liquid hydrocyanic acid, were determined. The molecular conductivities at the different dilutions, together with the molecular conductivities of these same substances in water, are given below :

Molecular Conductivities of KI at Zero.

In liquid HCN.		In H_2O.	
v.	μ_v.	v.	μ_v.
8	241	25.3	73.1
16	248	50.6	79.0
32	255	75.9	81.9
64	262		
128	268		
256	276		
512	282		
1024	289		

Molecular Conductivities of $S(CH_3)_3I$ at Zero.

In liquid HCN.		In H_2O.	
v.	μ_v.	v.	μ_v.
16	259	32	70.9
32	274	64	74.4
64	285	128	78.5
128	294	256	79.9
256	300		
512	307		
1024	311		

It is obvious from the above results that the conductivity of these substances in liquid hydrocyanic acid is several times greater than that in water at the same dilutions, and it is very probable that the dissociating power of this solvent is even greater than that of water. Before this conclusion could be accepted as final, the values of μ_∞ for the salts in hydrocyanic acid must be accurately determined. This conclusion, however, is made probable by the fact that the molecular conductivity increases very slowly with increase in dilution for the more dilute solutions studied, indicating that the value of μ_∞ had been very nearly reached in the most dilute solutions used. Centnerzwer concludes his paper with the observation that the dissociating power of this solvent, "together with the high value of its dielectric constant, furnishes a new confirmation of the Thomson-Nernst law of parallelism between dissociating power and dielectric constants."

This investigation is of special interest in that it makes it very probable that a solvent has been found which has a greater dissociating power than water. A number of attempts have been made to find such a solvent, and while it is possible that hydrogen dioxide may be a stronger dissociant than water, this is far from proved.

That this solvent conforms to the Thomson-Nernst hypothesis is also of interest, but it should be noted that while this hypothesis accords very beautifully with the theory of electrolytic dissociation, it is not a necessary consequence of the theory. If solvents, therefore, did not conform to the hypothesis it would not affect, in the slightest, the validity of the theory of electrolytic dissociation. HARRY C. JONES.

REVIEWS.

A LABORATORY GUIDE TO THE STUDY OF QUALITATIVE ANALYSIS. By E. H. S. BAILEY, PH.D., Professor of Chemistry, and HAMILTON P. CADY, A.B., Assistant Professor of Chemistry in the University of Kansas. Fourth edition. Philadelphia: P. Blakiston's Son & Co. 1901. pp. 234.

The object which the authors had in mind in preparing this work can be clearly seen by quoting a paragraph from their preface: "At the present time there seems to be an opportunity to broaden the methods of instruction in Qualitative Analytical Chemistry, and to teach not only the facts and the mechanical methods of carrying out the various operations of analysis, but also to render them more intelligible and interesting to the student, by a proper application of the theory of Electrolytic Dissociation and of the Mass Law. In the past we have had to be content with a bare statement of facts, which were largely unrelated, but the dissociation theory of Arrhenius and the law of mass action, as enunciated by Guldberg and Waage, have furnished us with a means of correlating and interpreting chemical phenomena."

The aim of this work is undoubtedly in the right direction. The theory of electrolytic dissociation, the law of mass action, the phase rule, and similar epoch-making generalizations have been frequently regarded as important in physical chemistry, but it has been held by many that it would be impossible, or at least undesirable, to introduce them into elementary courses in inorganic chemistry. In the last year or two a great change has been experienced. In 1900 the "Grundlinien der anorganischen Chemie" by Ostwald appeared, which showed how certain physical chemical conceptions can and ought to be introduced into general chemistry; and in the same year the "Lehrbuch der anorganischen Chemie," by Holleman, was published. The work of Holleman goes farther in certain directions than that of Ostwald, and, together with the latter, marks a new epoch in the development of inorganic chemistry.

That the principles which lie at the foundation of these works are finding practical application in the laboratory is shown by the appearance of a manual like the one in hand. Perhaps a little different treatment of certain subjects and a little fuller treatment of others would have been advantageous, but these are minor points. This book will undoubtedly contribute its share towards the application of physical chemical generalizations to inorganic chemistry.

The book is only about half the size that would be indicated by the number of pages, since half the pages are left blank for students' notes. H. C. J.

THE PRACTICAL METHODS OF ORGANIC CHEMISTRY. By LUDWIG GATTERMANN, PH.D., Professor in the University of Freiburg. Translated by WILLIAM B. SCHOBER, PH.D., Instructor in Organic Chemistry in Lehigh University. The second American from the fourth German edition. New York: The Macmillan Co. 1900.

The first edition of this book was reviewed in this JOURNAL[1] and attention was called to its excellence as a laboratory guide, combining as it does not only a very exact and thorough treatment of the details of the preparation of typical substances, but also in each case calling attention to the general principles involved and the general reactions of the substances, and the bearing of each case on others. In this edition a number of new preparations have been introduced, some of which have been devised since the last edition was published. The preparation of acetylene and acetylene tetrabromide have been omitted in this edition, no doubt owing to the fact that calcium carbide is now so accessible for the preparation of acetylene. This book should be in the hands of all who are teaching organic chemistry or are making organic preparations, as it is thoroughly up to date and more comprehensive and thorough than some of the books used for this purpose.

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[1] This JOURNAL, 19, 79.

J. E. G.

LEHRBUCH DER ANORGANISCHEN CHEMIE, FÜR STUDIERENDE AN UNIVERSITÄTEN UND TECHNISCHEN HOCHSCHULEN. Von DR. A. F. HOLLEMAN, o. Professor der Chemie an der Universität Groningen, in Gemeinschaft mit dem Verfasser bearbeitet und herausgegeben von DR. PHIL. WILHELM MANCHOT, Privatdocent der Chemie an der Universität Göttingen. Mit zahlreichen Abbildungen und zwei Tafeln. Verlag von Veit and Comp., Leipzig. 1900. pp. 439.

Less than two years ago the "Grundlinien der anorganischen Chemie," by Ostwald, appeared. This showed for the first time how physical-chemical generalizations can be applied to inorganic chemistry, and can, indeed, be made the basis of this branch of chemical science. In the same year the work in hand was published, which goes farther in certain directions than that of Ostwald. The way in which this book differs from the earlier works on inorganic chemistry can be seen best by reference to certain paragraphs.

After a consideration of ozone and hydrogen dioxide, the determination of molecular weights by the freezing-point and boiling-point methods is taken up. Having discussed hydriodic acid, the question of dissociation by heat is considered. In this connection the subjects of equilibrium in reactions in general and the order of reactions are entered into, and the equations both for first and second order reactions are developed. The theory of electrolytic dissociation is introduced after a number of the halogen acids have been studied. The phase rule is taken up in connection with sulphur, which furnishes such an excellent example of one substance existing in four phases. On page 136, after sulphur, selenium and tellurium, a chapter is devoted to thermochemistry and thermodynamics as applied to chemistry. Very much later in the work, after zinc, cadmium, and mercury have been taken up, a short chapter is devoted to electrochemistry, including a calculation of the electromotive force of primary cells, a discussion of the storage battery, the Leclanché element, etc.

It is obvious from the above that we have here also a departure from the text-books already existing in inorganic chemistry. Many of the fundamental conceptions of physical chemistry are introduced and applied to the phenomena of inorganic chemistry.

After a careful study of the book, the question may, however, be raised, Are these generalizations always introduced naturally into the subject, or are they forced in at certain places? In a few cases it must be confessed that they do not seem to fall naturally into the contents of the work, and in other cases it is a question whether these physical-chemical ideas have not been carried a little too far. Take the chapter on thermodynamics as applied to chemistry. This is so far above the level of the average reader of a book on inorganic chemistry that it will make but little impression upon him. But even here the question arises whether everything in a book should be written on the level of the average reader, or should the reader be required to make some effort to overcome difficulties which at first sight seem insurmountable?

These are, however, minor points. The main object of the work is excellent. It aims to introduce simple mathematical generalizations into inorganic chemistry, which is the first step toward placing chemistry upon the basis of an exact science. It is universally recognized that chemistry is much less fully developed than physics, and this has been attributed chiefly to the nature of chemical phenomena. These, as a whole, are more complex than physical phenomena, and, further, chemical reactions frequently proceed in steps, one part of A combining with one, two, three parts of B. Both of these influences have made it far more difficult to deal with the phenomena of chemistry by the only exact method, *viz.*, the mathematical.

It is one of the crowning glories of physical chemistry that these difficulties have been, at least in part, overcome, and many of the phenomena which twenty years ago were necessarily treated as empirical facts, can now be dealt with by rigid methods, and their meaning and significance seen.

The book in hand, together with Ostwald's "Grundlinien," undoubtedly marks a new epoch in the development of the science of inorganic chemistry. H. C. J.